

CANADIAN JOURNAL OF RESEARCH

VOLUME 14

JUNE, 1936

NUMBER 6

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NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

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Subscription rates, postage paid to any part of the world (effective 1 April, 1939), are as follows:

	<i>Annual</i>	<i>Single Copy</i>
A and B	\$ 2.50	\$ 0.50
C and D	2.50	0.50
Four sections, complete	4.00	—

The Canadian Journal of Research is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. All correspondence should be addressed:

National Research Council, Ottawa, Canada.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 14, SEC. A.

JUNE, 1936

NUMBER 6

THE HYPERFINE STRUCTURE OF LEAD III¹

By A. M. CROOKER²

Abstract

The hyperfine structures in the spectrum of Pb III, excited by an electrodeless discharge, have been studied by means of a 21 ft. concave grating. The hyperfine structure patterns lead to an I -value of $\frac{1}{2}$ and a $g(I)$ factor of 1.2 for the odd isotope Pb^{209} , in agreement with the results of previous workers. The isotope shifts between the even isotopes Pb^{208} and Pb^{206} are in agreement with Breit's theoretical interpretation, and amount to 0.5 cm^{-1} for each 6s electron. The fact that the deep terms in the spectrum of Pb III are rather completely known permits an attempt to be made at a careful comparison between experiment and theory.

Introduction

That hyperfine structure exists in the spectra of lead has been known for many years. Several strong arc lines were investigated in the period 1914-1922 by Richards and Lemberg and by Merton in an attempt to discover a difference in the spectra emitted by the isotopes of lead which occur separated in nature. The results of these experiments were inconclusive. In recent years, during the development of a fairly satisfactory theory of hyperfine structure in atomic spectra, the arc and first spark spectra of lead have been carefully reinvestigated by a number of workers. Kopfermann (10) first showed in a very clear way the effect of isotopic constitution upon hyperfine structure. He confirmed the rule used earlier by Schüler that the intensities of the hyperfine structure components due to the individual isotopes were proportional to their abundance ratio as determined by Aston. He showed further that the lead isotopes Pb^{206} (uranium) and Pb^{208} (thorium) contributed at most one component each to the hyperfine structure patterns, and he concluded that I and/or $g(I)$ was zero for these even isotopes. The isotope Pb^{207} (actinium) was shown to have a nuclear moment of $\frac{1}{2}$ atomic unit and a $g(I)$ factor of approximately 1.2.

These values have been verified by many other investigators working with the arc and first spark spectra. In these spectra, however, the interpretation of the experimental results is complicated by large perturbations between configurations of the same parity of the type discussed by Condon (4) and others. McLennan, Crawford and Leppard (13) have published a note on the hyperfine structure of Pb III in which they give the structure of $6s7s^3S_1$ and note the similarity of other structures to the corresponding ones in the isoelectronic spectrum Tl II. The present work was undertaken to extend these data.

¹ Manuscript received May 22, 1936.

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Experimental

The lines were excited, along with lines of Pb I, Pb II and Pb IV, by an electrodeless discharge in the vapor of ordinary lead at a temperature estimated to be about 600° C. (11). Under conditions favoring the excitation of Pb III the hyperfine structure components have a half-width of about 0.05 cm.⁻¹, and are therefore sufficiently narrow to permit the use of resolving powers of the order of several hundreds of thousands.

The data presented were obtained exclusively from plates taken with a 21 ft. concave grating, although several confirmatory plates were taken with a variable gap Fabry-Perot interferometer with 10 mm. separation and also a quartz Lummer plate. The plate holder of the grating is 13 ft. long and permits spectrograms to be obtained over the whole $n\lambda$ region from 12000 Å to 21000 Å in one exposure (5).

The dispersion at any arbitrary value of $n\lambda$ was obtained from the equations

$$\frac{d\lambda}{ds} = \frac{1}{n} \left[\frac{d}{R} \cos \theta \right] = \frac{1}{n} \left[\frac{d}{R} \left\{ 1 - \left(\frac{n\lambda}{d} - \sin i \right)^2 \right\}^{\frac{1}{2}} \right] \text{ Å per mm.} \quad (1)$$

$$\frac{dv}{ds} = n \left[\frac{10^8}{(n\lambda)^2} \frac{d}{R} \cos \theta \right] \text{ cm.}^{-1} \text{ per mm.,} \quad (2)$$

where d represents the grating space 16670 Å, R the radius of curvature 21.03 ft. = 6410 mm., and the angle of incidence $i = 31.5^\circ$. These formulas were checked against iron and neon standards and found to be consistently correct to within 0.1%. The expressions in brackets were calculated at $n\lambda$ intervals of 100 Å and entered in tabular form. The order of the line, n , was determined to establish a correspondence with the wave-length list obtained from excitation plates taken on Hilger E1 instruments with glass and quartz optical systems. In the grating used, the Rowland ghosts amount to about 2% of the intensity of the main line in the third order. These ghosts are symmetrically situated with respect to the main line and separated from it by

$$\Delta\lambda = \frac{k\lambda}{np}, \quad (3)$$

where n is the order of the main line, k that of the ghost, and p the number of rulings involved in the periodic error responsible for the ghosts which is 300 in the present grating. From Equation (1) the separation between the Rowland ghosts in millimetres may be derived—

$$\Delta s = \frac{\lambda}{300} \left[\frac{R}{d} \frac{1}{\cos \theta} \right]. \quad (4)$$

It is very convenient to use this formula to aid in eliminating the ghosts.

Altogether five exposures were made on Ilford Special Rapid Panchromatic plates with exposures varying from two to four hours. In addition to these, one exposure of eight hours was obtained with Schumann, and one of fourteen hours with hypersensitized Eastman 3-Q infra-red, plates. The extreme wave-lengths recorded were 2117 and 6660 Å. All the lines occurring on one

series of Ilford plates were identified and measured on a Hilger comparator reading to 0.001 mm. The lines showing hyperfine structure were measured at least five times in both directions. This procedure of measuring the hyperfine structure was repeated on the Schumann plates and in certain cases on other Ilford plates. The Eastman plates showed very strong halation and served only to check the weaker components. It was necessary to exercise considerable care in order to obtain consistent measurements, as the structures are narrow, of the order of 1 cm.⁻¹, and the intensities of the components differ considerably. It was rarely necessary to use measurements from both a long and a short exposure to arrive at the structure of a line. The Schumann plates were used to minimize the effect of errors due to developer and gelatin. It is believed that the average probable error in the measured separations of the hyperfine structure components is about 0.01 cm.⁻¹. The separations in several lines are certainly more accurate than this. The dispersion varies from about 3 to 6 cm.⁻¹ per mm.

In one exposure on Ilford plates, light from an iron arc was passed axially through the discharge tube after a normal exposure of lead spectra had been made. This method of procedure introduced no relative shift between the iron and the lead lines. The lead lines were then measured with respect to the iron lines as standards, the calculated dispersions and the method of coincidences being used. As the $n\lambda$ values of the iron lines were usually correct to within 0.02 Å, it appears that the wave-lengths of the lead lines may be expected to be correct to within 0.01 Å. This accuracy allows the frequencies of the hyperfine components of any line pattern to be given to within 0.05 cm.⁻¹. The frequency analysis substantiates these estimates of the probable errors.

Results and Interpretation

The hyperfine structure of the Pb III lines investigated are presented in Table I. In this table Column 1 gives the wave-lengths of the even isotope components Pb²⁰⁶ and Pb²⁰⁸. Columns 2 and 3 give respectively the corresponding frequencies and the classification of the line. The evidence for

TABLE I
HYPERFINE STRUCTURE OF Pb III LINES

λ I.A.	ν , cm. ⁻¹	Classification	Hyperfine structure components, cm. ⁻¹	$\frac{\text{Pb}^{207} - \text{Pb}^{206}}{\text{Pb}^{208} - \text{Pb}^{206}}$
5857.96	17066.05	$6s6d\ ^3D_3 - 6s7p\ ^3P_2^0$	(20) Unresolved (30) (0) 6.05 7.50	
5779.41	17298.00	$6s7s\ ^1S_0 - 6s7p\ ^3P_1^0$	(0) (10) (1) 6.76 8.00 8.62	
5523.97	18097.90	$6s6d\ ^3D_3 - 6s7p\ ^3P_2^0$	(0) (3) (6) (0) 7.48 7.84 7.96 8.18	.50
5275.76 .63	18949.35 .80	$6s6d\ ^3D_3 - c\ 6_2^2$	(1) (3) (6) (0) 9.03 9.34 49.81 50.15	.38

TABLE I—Continued
HYPERFINE STRUCTURE OF Pb III LINES—Continued

λ I.A.	ν , cm. ⁻¹	Classification	Hyperfine structure components, cm. ⁻¹				$\frac{\text{Pb}^{207} - \text{Pb}^{206}}{\text{Pb}^{208} - \text{Pb}^{206}}$	
5207.78 .70	19196.70 7.00	$6s6d\ ^1D_2 - 6s7p\ ^3P_1^0$	(0)?	(2) 6.70	(4) 7.00	(1) 7.31	.33	
5191.56	19256.70	$6s6d\ ^3D_2 - 6s7p\ ^1P_1^0$	(1) 6.19	(3) 6.60	(6) 6.81	(0) 7.49		
5065.12	19737.40	$6s6d\ ^3D_1 - 6s7p\ ^1P_1^0$		(1) 7.27	(3) 7.53			
4855.12 .00	20591.08 .63	$6p^2\ ^2P_1 - 6s7p\ ^3P_2^0$	(0) 0.36	(2) 1.08	(5) 1.63			
4826.86	20711.60	$6s7p\ ^1P_1^0 - 6s8s\ ^3S_1$	(1) 0.68	(10) 1.60				
4802.34 .27	20817.40 .70	$6s7s\ ^1S_0 - c\ 5_1^0$		(8) 7.40	(12) 7.70			
4798.59	20833.65	$6s7s\ ^3S_1 - 6s7p\ ^3P_2^0$	(4) 2.90	(20) 3.65	(2) 4.204			
4761.12	20997.60	$6s7s\ ^3S_1 - 6s7p\ ^3P_1^0$	(1) 5.615	(20) 7.60	(2) 7.92	(1) 9.77		
4596.52 .38	21749.50 50.18	$6p^2\ ^2P_1 - 6s7p\ ^1P_1^0$		(0) 9.50	(1) 0.18			
4571.21	21869.93	$6s7p\ ^3P_2^0 - 6s8s\ ^3S_1$	(2) 9.33	(12) 9.93	(4) 0.10	(0) 1.48		
4499.36 .32	22219.16 .38	$6s7p\ ^1P_1^0 - 6s8s\ ^1S_0$		(5) 9.16	(3) 9.38			
4400.94 .83	22716.05 .60	$6s6d\ ^1D_2 - c\ 5_1^0$		(8) 6.05	(12) 6.60			
4272.66	23398.06	$6s7s\ ^1S_0 - 6s7p\ ^1P_1^0$	(2) 7.87	(12) 8.06	(1) 8.44			
4219.90 .81	23690.58 1.05	$c\ 6_2^0 - 6s7d\ ^3D_2$		(2) 0.58	(1) 1.05			
4182.51 .44	23902.30 .70	$6s7s\ ^3S_1 - c\ 4_2^0$	(1) 1.34	(9) 1.90	(20) 2.30	(30) 2.70	(4) 3.64	.38
4181.82 .75	23906.30 .70	$c\ 4_2^0 - 6s8s\ ^3S_1$	(0) 5.49	(4) 6.29	(2) 6.72	(1) 7.05		.35
4141.31 .23	24140.17 .63	$c\ 6_2^0 - 6s7d\ ^3D_2$	(1) 9.82	(7) 0.165	(4) 0.63	(2) 0.99		.35
4128.11	24217.35	$6s7p\ ^1P_1^0 - 6s7d\ ^3D_1$		(6) 7.25	(2) 7.45			
4094.55 .52	24415.80 6.00	$6s7p\ ^1P_1^0 - 6s7d\ ^3D_2$	(1) 4.93	(5) 5.79	(3) 6.015	(2) 6.52		.42
4077.65 .60	24517.00 .30	$6s7s\ ^3S_1 - c\ 5_1^0$	(1) 6.32	(2) 7.01	(4) 7.29	(0) 8.63		.29

TABLE I—Continued
 HYPERFINE STRUCTURE OF Pb III LINES—Continued

λ I.A.	ν , cm. ⁻¹	Classification	Hyperfine structure components, cm. ⁻¹				$\frac{\text{Pb}^{207} - \text{Pb}^{206}}{\text{Pb}^{208} - \text{Pb}^{206}}$
4031.19 .14	24799.30 .60	$c\ 5^{\circ}_1 - 6s8s\ ^1S_0$	(4) 9.30	(2) 9.61			
4004.16 .11	24967.00 .30	$6p^2\ 3_2 - 6s5f\ ^3F^{\circ}_3$	(3) 6.99	(5) 7.31			
3951.97 .88	25296.71 7.18	$6s6d\ ^1D_2 - 6s7p\ ^1P^{\circ}_1$	(2) 6.61	(4) 6.71	(8) 7.18	(1) 7.45	
3854.08	25939.20	$6s7s\ ^3S_1 - 6s7p\ ^3P^{\circ}_2$	(1) 7.60	(9) 8.98	(30) 9.20	(5) 9.90	
3841.53	26023.94	$6s7p\ ^3P^{\circ}_2 - 6s7d\ ^3D_3$	(2) 2.46	(30d) 3.94			
3832.82 .77	26083.10 .40	$6p^2\ 3_2 - 6s5f\ ^1F^{\circ}_3$	(20) 3.08	(30) 3.43			
3827.40 .37	26120.00 .20	$6s7p\ ^1P^{\circ}_1 - 6s7d\ ^1D_2$	(20) 0.00	(12) 0.21			
3739.76	26732.10	$6s5f\ ^1F^{\circ}_3 - 6s5g\ 6_4$	(4) 1.38	(30) 2.10	(3) 2.92		
3735.96	26759.30	$6s5f\ ^1F^{\circ}_3 - 6s5g\ 9_4$	(3) 8.76	(30) 9.30	(4) 9.80		
3728.69	26811.47	$6s7p\ ^3P^{\circ}_1 - 6s8s\ ^3S_1$	(1) 9.41	(15) 1.47	(1) 3.41		
3706.02	26975.50	$6s7p\ ^3P^{\circ}_1 - 6s8s\ ^3S_1$	(1) 4.07	(12) 5.50	(2) 6.21		
3689.31	27097.65	$6s7s\ ^3S_1 - 6s7p\ ^1P^{\circ}_1$	(5) 6.73	(12) 7.60	(15) 7.75	(1) 9.02	(2) 9.59
3674.83	27204.43	$6s5f\ ^3F^{\circ}_4 - 6s5g\ 6_4$	Single (2)				
3671.36	27230.10	$6s5f\ ^3F^{\circ}_4 - 6s5g\ 8_8$	Single (30)				
3671.16	27231.56	$6s5f\ ^3F^{\circ}_4 - 6s5g\ 9_4$	Single (2)				
3655.60	27347.53	$6s5f\ ^3F^{\circ}_3 - 6s5g\ 7_3$	Single (15)				
3620.75 .69	27610.70 1.10	$c\ 4^{\circ}_2 - 6s7d\ ^3D_2$	(4) 0.70	(2) 1.15			
3593.18 .13	27822.60 3.00	$6s7s\ ^3S_1 - c\ 6^{\circ}_2$	(0) 1.75	(4) 2.17	(9) 2.60	(15) 3.02	(2) 4.06
3589.87	27848.2	$6s5f\ ^3F^{\circ}_3 - 6s5g\ 6_4$	(4) 7.59	(20) 8.20	(3) 8.85		
3589.63	27850.1	$6s5f\ ^3F^{\circ}_3 - 6s5g\ 7_3$	(0) 9.55	(4) 0.10	(0) 0.80		
3586.37	27875.4	$6s5f\ ^3F^{\circ}_3 - 6s5g\ 9_4$	(3) 4.68	(20) 5.40	(4) 6.02		

.40

TABLE I—*Concluded*
HYPERFINE STRUCTURE OF Pb III LINES—*Concluded*

λ I.A.	ν , cm. ⁻¹	Classification	Hyperfine structure components, cm. ⁻¹	$\text{Pb}^{207} - \text{Pb}^{206}$ $\text{Pb}^{208} - \text{Pb}^{206}$
3562.73 .67	28060.4 .8	$c\ 4\frac{1}{2}_2 - 6s7d\ ^3D_3$	(2) (8) (5) (3) 0.13 0.40 0.84 1.13	
3530.17	28319.2	$6s7p\ ^3P_1^o - 6s8s\ ^1S_0$	(1) (5) (0) 8.59 9.20 0.42	
3483.27 .22	28700.5 .9	$c\ 5\frac{1}{2}_1 - 6s7d\ ^1D_2$	(12) (8) 0.50 0.86	
3297.50	30317.30	$6s7p\ ^3P_1^o - 6s7d\ ^3D_1$	(2) (15) (0) (1) 6.36 7.30 8.20 9.22	
3279.76	30481.3	$6s7p\ ^3P_0^o - 6s7d\ ^3D_1$	(2) (10) (1) 0.93 1.30 1.95	
3279.41 .37	30484.5 .9	$6s7s\ ^1S_0 - c\ 8\frac{1}{2}_1$	(9) (15) 4.50 4.90	
3276.05	30515.8	$6s7p\ ^3P_1^o - 6s7d\ ^3D_2$	(0) (4) (20) (2) 4.56 5.60 5.80 6.41	
3242.84	30828.3	$6s6d\ ^3D_3 - 6s5f\ ^3F_3^o$	(3) (20) (2) 7.63 8.30 9.12	
3176.50	31472.1	$6s6d\ ^3D_3 - 6s5f\ ^3F_2^o$	(1) (15) 0.70 2.10	
3137.81	31860.15	$6s6d\ ^3D_2 - 6s5f\ ^3F_3^o$	(3) (20) (2) 9.83 0.15 0.57	
3102.74	32220.25	$6s7p\ ^3P_1^o - 6s7d\ ^1D_2$	(2) (10) (1) 9.47 0.25 1.81	
3089.08	32362.70	$6s6d\ ^3D_2 - 6s5f\ ^3F_2^o$	(3) (20) (0) (2) 1.98 2.70 2.98 3.72	
3087.12 .05	32383.28 4.00	$6s6d\ ^1D_2 - c\ 8\frac{1}{2}_1$	(2) (4) 3.28 4.00	
3043.85	32843.6	$6s6d\ ^3D_1 - 6s5f\ ^3F_2^o$	(30) (2) 3.60 4.52	
2868.09 .05	34856.2 .7	$6p^2\ 2_1 - 6s5f\ ^3F_2^o$	(1) (2) 6.2 6.7	
2638.43 .41	37889.8 90.3	$6s6d\ ^3D_3 - c\ 10\frac{3}{2}_2$	(1) (2) 9.80 0.30	
2568.52 .49	38921.30 .80	$6s6d\ ^3D_2 - c\ 10\frac{3}{2}_2$	(2) (4) 1.30 1.80	
2562.24 .23	39016.60 .80	$6s6d\ ^1D_2 - 6s5f\ ^1F_3^o$	(15) (20) 6.60 6.82	
2117.49 .47	47210.70 1.10	$6s6p\ ^1P_1^o - 6p^2\ 1_0$	(2) (1) 0.70 1.10	

the allotted term assignments is discussed in a separate paper (12). The terms arising from the configuration $5d^9 6s^2 6p$ are designated "c" for brevity. In Column 4 are given the last three figures of the frequencies of the hyperfine structure components to within 0.01 cm^{-1} . The red components are to the left. The value of the frequency of the components of any hyperfine structure pattern may be in error by 0.05 cm^{-1} , but the hyperfine structure separations of the components are believed to be correct to within 0.01 cm^{-1} . The relative intensities of the components as estimated visually are given above the measured positions and are enclosed in parentheses. Concerning these it should be stated that while the intensities within one pattern are careful estimates, the strong patterns are considerably stronger with respect to the weaker patterns than the intensities given would indicate. The ratio of the separation of the centre of gravity of the Pb^{207} pattern from the isotope line Pb^{206} to the total separation between the components due to the isotopes Pb^{208} and Pb^{206} is presented in Column 5.

In interpreting the hyperfine structure patterns it is essential to keep clearly in mind the isotopic constitution of ordinary lead which is given by Aston (1) as $\text{Pb}^{204} : \text{Pb}^{206} : \text{Pb}^{207} : \text{Pb}^{208} = 1.50 : 27.75 : 20.20 : 49.55$. In a completely resolved pattern showing isotope shift, the two strongest components belong to Pb^{208} and Pb^{206} . No definite evidence was obtained of the existence of Pb^{204} in this work.

Hyperfine structure term separations deduced from the observed line patterns are given in Table II. The relative term values given in Column 2 represent the average of the Pb^{206} and Pb^{208} values. This mean value coincides with the centre of gravity of the Pb^{207} terms and gives, to within the error of measurement, the measured centre of gravity of lines in which the isotope shifts are not resolved. Actually these two so-called centres of gravity lie on opposite sides of the mean term value of Pb^{206} and Pb^{208} , since the centre of gravity of the Pb^{207} terms lies closer to Pb^{206} , but are rarely separated from the mean term value by more than 0.05 cm^{-1} .

TABLE II
HYPERFINE STRUCTURE OF Pb III TERMS

Term	Term value, cm^{-1} ($6s^2 \text{ } ^1S_0 = 0$)*	Total separation, cm^{-1}	Interval factor, A, cm^{-1}	Isotope shift,† cm^{-1}
<i>Odd</i>				
$6s6p \text{ } ^1P_1^o$	95338.9			.05
$6s7p \text{ } ^3P_1^o$	171079.45	1.85	1.23	.05
<i>c</i> 4_2^o	173984.45	.57	.23	.46
<i>c</i> 5_1^o	174599.0	~0.	~0.	.35
$6s7p \text{ } ^3P_2^o$	176021.05	1.39	.55	.12
$6s7p \text{ } ^1P_1^o$	177179.5	— .57	— .38	.20

TABLE II—*Concluded*
 HYPERFINE STRUCTURE OF Pb III TERMS—*Concluded*

Term	Term value, cm. ⁻¹ (6s ² ¹ S ₀ = 0)*	Total separation, cm. ⁻¹	Interval factor, A, cm. ⁻¹	Isotope shift,† cm. ⁻¹
c 6 ₂ ^o	177904.6	.41	.16	.46
c 8 ₁ ^o	184266.3	~ - .3	~ - .2	.45
6s5f ³ F ₂ ^o	189783.3	~0.	~0.	Small
³ F ₂ ^o	190285.9	-1.00	- .40	.06
³ F ₄ ^o	190427.1	1.4	.31	Small
¹ F ₃ ^o	190899.4	.3	.09	.04
Even 6p ² 1 ₀	142549.8	0.	0.	-.35
6s7s ³ S ₁	150081.85	2.30	1.53	.06
6s6d ¹ D ₂	151882.65	.28	.11	-.27
6s7s ¹ S ₀	153781.45	0.	0.	.06
6p ² 2 ₁	155429.7	-0.		-.44
6s6d ³ D ₁	157442.3	- .9	- .6	-.06
³ D ₂	157923.2	.73	.29	-0.
³ D ₃	158955.0	1.53	.44	0.
6p ² 3 ₂	164816.15	Small		-.32
6s8s ³ S ₁	197891.0	2.145	1.43	.03
6s8s ¹ S ₀	199398.6	0.	0.	.03
6s7d ³ D ₁	201396.8	-1.02	- .68	0.
³ D ₂	201595.3	1.04	.41	0.
³ D ₃	202045.0	1.58	.45	0.
¹ D ₂	203299.65	- .48	- .19	0.
6s5g 6 ₄	217631.5	-1.25	- .28	Small
7 ₃	217633.4	-1.25	- .36	Small
6s5g 8 ₆	217657.2	~1.4	~ .25	Small
9 ₄	217658.7	1.34	.30	Small

* The absolute term value of 6s² ¹S₀ is estimated to be 257690 cm.⁻¹ with respect to 6s ²S_{1/2} of Pb IV.

† A positive value for the isotope shift means that Pb²⁰⁶ lies deeper than Pb²⁰⁸ when the 6s7d terms (or ionization limits) of the two isotopes are made to coincide. If the 6s² ¹S₀ terms are arbitrarily brought into coincidence, then approximately 0.5 cm.⁻¹ is subtracted from all the shifts, that is, when the ground states of the two even isotopes are made to coincide the Pb²⁰⁶ levels lie uniformly higher than the Pb²⁰⁸ levels.

Theoretical Discussion

In this section the hyperfine structure term separations given in Table II are shown to be in fair agreement with the multiplet analysis and the theory of hyperfine structure.

(a) The Magnetic Hyperfine Structure Due to Pb²⁰⁷

Since all terms are split into two hyperfine structure levels, except the terms with $J = 0$ which are single, it can immediately be concluded that $I = \frac{1}{2}$. This conclusion is supported by intensity considerations, and is in agreement with previous work.

That perturbations are present is evident from the distribution of the multiplet terms. Thus the odd configurations $6s6p$, $6s7p$ and $6s5f$ are all mutually perturbed by the terms from the intermixed configuration $5d^96s^26p$. Similarly the even configurations $6s6d$ and $6p^2$ overlap and perturb each other strongly. An unidentified term, possibly from $5d^96s^26d$, must be invoked to explain the anomalous multiplet and hyperfine structure present in terms arising from the configuration $6s5g$. Unique configuration assignments have been made in these cases which appear to characterize best the observed position, hyperfine structure and isotope shift.

These perturbations render the terms involved of little use for the calculation of the nuclear magnetic moment, as usually the hyperfine structure is known for an insufficient number of terms to permit an application of the sum rule. However the terms $6s7s\ ^3S_1$, $6s6d\ ^3D_3$, $6s8s\ ^3S_1$ and $6s7d\ ^1,^3D$ are all available for the calculation of the nuclear moment. The fact that these terms are well distributed permits a fairly satisfactory extrapolation of the interaction constant of the $6s$ electron to that of the $6s\ ^2S_{\frac{1}{2}}$ state of Pb IV.

For the interaction constant of such a single s electron Fermi and Segrè (6) have given the expression,

$$a = 15.5 \frac{g(I)}{1838} \frac{1}{(1 - \beta^2 Z_i^2)^2} \frac{Z_i z_0^2}{n^{*3}} \left(1 - \frac{\partial s}{\partial n}\right) \text{cm.}^{-1}, \quad (5)$$

where $(1 - \beta^2 Z_i^2)^{-2}$ is a relativistic correction factor with $\beta = 1/139$; Z_i and z_0 measure the effective nuclear charge in the inner and outer regions; n^* is the effective quantum number, and the last factor arises from the fact that the quantum defect s of the 2S sequence decreases as n increases.

For two s electrons the interval factor is known to be half the sum of the individual interaction constants

$$A(^3S_1) = \frac{1}{2}(a_1 + a_2). \quad (6)$$

By means of this expression and Equation (5) the following estimates were made of the interaction constants involved in $6s7s\ ^3S_1$ and $6s8s\ ^3S_1$.

$$\text{In } 6s7s\ ^3S_1: a_{6s} = 2.5; a_{7s} = .58$$

$$\text{In } 6s8s\ ^3S_1: a_{6s} = 2.6; a_{8s} = .26.$$

Breit and Wills (3) have given formulas for several two electron configurations including those of the type $6s7d$. The expressions for the interval factors of the terms of such configurations which are independent of coupling are

$$\left. \begin{aligned} A({}^3L_{l+1}) &= \frac{a(s)}{2(l+1)} + \frac{l+\frac{1}{2}}{l+1} a' \\ A({}^3L_{l-1}) &= \frac{-a(s)}{2l} + \frac{l+\frac{1}{2}}{l} a'' \end{aligned} \right\} \quad (7)$$

where a' and a'' refer to the interaction constant of the non- s electron with $J = l + \frac{1}{2}$ and $l - \frac{1}{2}$ respectively. They are related to the constant

$$a = \frac{2g(I)}{1838} \frac{\mu_0^2}{hc} \left(\frac{1}{r^3} \right) \text{ cm.}^{-1}$$

by the relations

$$a : a' : a'' = \frac{l+\frac{1}{2}}{l(l+1)} : \frac{1}{l+3/2} : \frac{1}{(l-\frac{1}{2})}$$

in the unrelativistic approximation. In the present case, however, the contribution of the $7d$ electron may be neglected, and there is thus obtained for the interaction constant of the $6s$ electron in $6s6d {}^3D_3$, $6s7d {}^3D_1$ and $6s7d {}^3D_3$ the values 2.64, 2.72 and 2.70 respectively.

Breit and Wills (3) have also given formulas for the two levels in $6s7d$ which are dependent on coupling in terms of a coupling parameter θ . Racah (14) had previously considered the same problem, but his formulas allow the relativistic correction to be made for the non- s electron only in the case of (jj) coupling. As it is possible to neglect entirely the contribution of the $7d$ electron in the configuration $6s7d$, Racah's formulas may be used. They may be written in the form

$$\left. \begin{aligned} A({}^3L_l) &= \left\{ (g_3 - 1) + 2\delta \right\} \frac{a(s)}{2} + (1 + \delta)a \\ A({}^1L_l) &= \left\{ (g_1 - 1) - 2\delta \right\} \frac{a(s)}{2} + (1 - \delta)a \end{aligned} \right\} \quad (8)$$

where $a(s)$ and a are as defined above, g_3 and g_1 are the Landé g -factors of the "triplet" and "singlet" levels calculated from Houston's equations (8) and

$$\delta = \frac{{}^3L_{l+1} - {}^3L_{l-1}}{(2l+1)({}^1L_l - {}^3L_l)}.$$

The $6s7d$ multiplet satisfies Houston's equations remarkably well, and g_3 , g_1 and δ are respectively 1.161, 1.006 and 0.076. Thus there are obtained for the interaction constant of $6s$ in $6s7d {}^3D_2$ the value of 2.62, and in $6s7d {}^1D_2$ the value 2.60. The terms $6s5g {}^7_3$ and 8_5 must be perturbed, as the separation between them is of the order of 10 times the $5g {}^2G$ difference in Pb IV. The interaction constant of the $6s$ electron derived from the hyperfine structure separations of these terms is 2.88 and 2.55, respectively. Not much weight can be given to these values, for the hyperfine structures are somewhat uncertain.

Following Goudsmit (7), we may now extrapolate to obtain 2.8 cm^{-1} as a plausible value for $a(s)$ in $6s \text{ } ^2S_{1/2}$ of Pb IV for which $n^* = 2.267$. From this

$$g(I) = \frac{2.8 \times 1838 \times 11.7}{15.5 \times 2.36 \times 82 \times 16 \times 1.08} = 1.16,$$

where the origin of the separate factors is evident from Equation (5).

Fermi and Segrè (6) use a different method, extrapolating to obtain both the interaction constant and the effective quantum number of a $6s$ electron in $6s^2 \text{ } ^1S_0$. With the values 2.4 cm^{-1} and 1.9 for these respectively

$$g(I) = \frac{2.4 \times 1838 \times 6.86}{15.5 \times 2.36 \times 82 \times 9 \times 1.08} = 1.04.$$

As it is essentially the same results that are being treated in these two cases, it appears that the arbitrariness in the method of reducing the data is great. The method of extrapolation used by Goudsmit appears to have some advantages, and would be more satisfactory if some quantitative estimate could be made of the way in which the interaction constant of a $6s$ electron, say, increases with the relative term value in such a spectrum as Pb III. Such an estimate of the change in "screening" would at present involve a long, uncertain and difficult calculation.

(b) *The Hyperfine Structure Due to Isotope Shift*

In discussing isotope shift effects it must be kept clearly in mind that the term systems of the several isotopes are quite independent, so that it is always necessary to state clearly which levels have been arbitrarily brought into coincidence. That the large isotope shifts, at least in the spectra of the heavy elements, are found in lines due to transitions between terms arising from configurations involving a different number of s electrons, has been known for several years. Breit (2) seems to have first understood that, referred to a term from an arbitrary configuration, a term from a configuration with more s electrons showed the lighter isotope deeper, and similarly that a term from a configuration with fewer s electrons showed the heavier isotope deeper. This rule holds quite generally in the spectra of heavy atoms, and Breit (2) has shown that a consistent interpretation of the magnitude of the shifts observed in the spectra of mercury, thallium and lead is obtained by assigning to each $6s$ electron a shift of approximately 0.5 , 0.25 and 0.5 cm^{-1} respectively, in these spectra. Further, the isotope displacements recently observed by Jaeckel and Kopfermann (9) in the spectrum of Pt I can be accounted for in this way by attributing a shift of 0.1 cm^{-1} to each $6s$ electron per two mass units (neutrons).

From Breit's theory of isotope displacement it is expected, for a given nucleus, that the shift will be proportional to the interaction constant of the s electron involved, as both contain $\psi^2(0)$ as a factor. Now, in support of this it is known that the observed shifts are larger in higher ionizations, but in Pb III there is a suggestion that, with increasing quantum number, the isotope shift decreases more rapidly than the interaction constant.

The measurements are hardly accurate enough to assign much weight to the values obtained for the position of the centre of gravity of the Pb^{207} isotope levels relative to the two even isotope levels. The measurements indicate a value of about 0.36 for the ratio $(\text{Pb}^{207}-\text{Pb}^{206})/(\text{Pb}^{208}-\text{Pb}^{206})$, in fair agreement with the measurements of Rose (15) who obtains 0.40, and Schöler and Jones (16) who obtain 0.30.

Acknowledgments

The writer wishes to thank Prof. E. F. Burton, Director of the McLennan Laboratory, for his friendly interest, and Mr. M. F. Crawford for many helpful discussions and his generosity in undertaking the correction of the proofs. The interpretation of the data was completed while the writer was an 1851 Exhibition research student at King's College, University of London, under the direction of Prof. O. W. Richardson.

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Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 14, SEC. B.

JUNE, 1936

NUMBER 6

THE CONDUCTIVITY OF ALKALI-WATER-ACETONE SOLUTIONS¹

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Abstract

Increased acetone concentration in aqueous solutions of sodium hydroxide lowers the specific conductivity to a marked degree. This cannot be satisfactorily explained by viscosity change only, but is probably accounted for by a combination of changes in both viscosity and dielectric properties of the solutions. An empirical equation is suggested.

Introduction

In the course of an investigation into the mechanism of the Messenger method of estimating acetone (11), the importance of the order of addition of reagents and of the alkali concentration suggested the study of ionic behavior in such solutions.

In outline the idea was to find the conductivities of various acetone-sodium hydroxide-water mixtures. Such data as were available on electrolytes in mixed solvents dealt mainly with alcohol-water systems. It was therefore decided to proceed along the above lines.

Materials

Hydrochloric acid. This was prepared according to the method of Bonner and Hulett (4), and made up to normal and decinormal.

Sodium hydroxide. Normal and decinormal solutions were prepared carbonate-free.

Acetone. C.p. material was made just alkaline and distilled; two further fractionations gave material of satisfactory boiling point.

Water. This was obtained chemically pure after several distillations, but was not exactly "conductivity water", which was unnecessary.

Experimental

Complete data for purposes of calculation later involved a series of procedures which are given below.

I. Volume Change

After preliminary trials the procedure finally adopted was to pipette quantities of the various materials into a 160 cc. flask whose neck was a piece of shellback burette, closed by a stopper. Since all conductivity measurements

¹ Manuscript received April 22, 1936.

Contribution from the Department of Chemistry, McGill University, Montreal, Canada. From a thesis presented in partial fulfilment of the requirements for the Ph.D. degree at McGill University, Montreal.

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were to be made at 0° C., these materials were kept in an ice-water bath, as was also the dilatometer flask, which had been carefully calibrated. After addition of the materials, the stoppered flask was inverted three times, a stop watch was started and readings of the volume were made at suitable intervals until equilibrium was reached.

In Table I are found the values for the volumes finally obtained on mixing aqueous sodium hydroxide, aqueous acetone, and water at 0° C. The concentrations are moles per litre.

TABLE I
VOLUME CHANGE WITH CONCENTRATION

No.	NaOH	C ₃ H ₈ O	Additive volume, cc.	Final volume, cc.
17	1.310	0.880	160	158.5
18	0.566	0.880	160	158.7
19	0.254	0.880	160	158.8
20	0.109	0.880	160	158.9
21	0.053	0.880	160	158.9
22	0.050	1.780	160	157.8
23	0.102	1.780	160	157.8
24	0.238	1.780	160	157.7
25	0.532	1.780	160	157.6
26	1.230	1.780	160	157.6
27	0.994	4.500	160	153.7
28	0.426	4.500	160	154.5
29	0.191	4.500	160	154.6
30	0.083	4.500	160	154.6
31	0.040	4.500	160	154.7

The error of these measurements was not more than 1 in 1600.

II. Viscosities of Mixtures

These were determined with a modified form of Ostwald viscosimeter, and all measurements were made at 0° C. Table II shows the concentrations of

TABLE II
VISCOSITY AND CONCENTRATION

No.	NaOH	C ₃ H ₈ O	Viscosity of NaOH	Viscosity of C ₃ H ₈ O—NaOH—H ₂ O
17	1.310	0.880	1.33	1.62
18	0.566	0.880	1.11	1.30
19	0.254	0.880	1.04	1.18
20	0.109	0.880	1.02	1.18
21	0.053	0.880	1.01	1.18
22	0.050	1.780	1.01	1.34
23	0.102	1.780	1.02	1.37
24	0.238	1.780	1.04	1.43
25	0.532	1.780	1.10	1.55
26	1.230	1.780	1.29	1.83
27	0.994	4.500	1.21	2.57
28	0.426	4.500	1.08	2.12
29	0.191	4.500	1.03	1.93
30	0.083	4.500	1.02	1.84
31	0.040	4.500	1.01	1.81

alkali and acetone, the specific viscosity of alkali-water mixtures and finally the specific viscosity of acetone-alkali-water mixtures.

The values given in Tables I and II were plotted graphically against concentrations, so as to have them available for the conductivity work.

III. Conductivity of Mixtures

After a number of trials, a glass cell was devised to suit the requirements of temperature control, etc. Briefly, it consisted of an irregular U-tube with sealed-in platinum electrodes, the bottom being of much smaller bore than the sides, and one arm having a stopcock for rapid emptying and cleaning. The electrodes were platinized before use.

In the electrical set-up were a microphone hummer of 1000 cycles frequency, a telephone receiver similarly tuned, a variable resistance of 1 to 41,000 ohms and a slide wire readable to 1 in 1000.

Because of the comparative nature of the results desired, capacity and inductance were ignored as their effects were found to be negligible.

The cell constant was determined at 0° C. with *N*, *N*/10 and *N*/100 solutions of potassium chloride. It was found that the cell constant changed 0.4 unit for a variation of 12,400 ohms. The resistance was plotted against the cell constant and the latter read off from the curve obtained.

In making the mixtures, the solutions were mixed (as given under I), cooled for 30 sec., the cell was rinsed out with this solution, then filled, and the first resistance reading made three minutes after the initial mixing; readings were then continued until a final value, which represented the end of any volume or temperature effect, was obtained.

Table III shows the molar concentrations of alkali and acetone, initial and final conductivities of the acetone-alkali mixture, and finally the conductivity of the same concentration of sodium hydroxide in water alone.

TABLE III
SPECIFIC CONDUCTIVITY AND CONCENTRATION

No.	NaOH	C ₂ H ₆ O	Conductivity, NaOH	Conductivity of mixture	
				Initial	Final
17	1.310	0.880	0.1260	0.1090	0.1070
18	0.566	0.880	0.0634	0.0572	0.0554
19	0.254	0.880	0.0306	0.0273	0.0265
20	0.109	0.880	0.0136	0.0125	0.0123
21	0.053	0.880	0.0068	0.0062	0.0060
22	0.050	1.780	0.0066	0.0050	0.0049
23	0.102	1.780	0.0132	0.0103	0.0095
24	0.238	1.780	0.0290	0.0222	0.0213
25	0.532	1.780	0.0598	0.0466	0.0448
26	1.230	1.780	0.1224	0.0880	0.0856
27	0.994	4.500	0.1044	0.0427	0.0406
28	0.426	4.500	0.0500	0.0232	0.0218
29	0.191	4.500	0.0238	0.0112	0.0107
30	0.083	4.500	0.0106	0.0053	0.0050
31	0.040	4.500	0.0054	0.0028	0.0025

Examination of Table III shows that $\frac{\text{initial conductivity}}{\text{final conductivity}}$ rises regularly from 1.02 in No. 17 to 1.09 in No. 31. If the concentrations in Table III be plotted against final conductivity, it will be observed that the conductivity varies as the concentration of alkali, with a fixed concentration of acetone; and also as the concentration of acetone with the concentration of alkali a constant.

To make sure that the effects noted previously were not specific for sodium hydroxide, some of the experiments were repeated with potassium hydroxide as the alkali. Identical results were obtained.

IV. Freezing Points of Mixtures

These were obtained in the usual Beckmann apparatus, and the results are shown in Tables IV and V.

TABLE IV
WITH SODIUM HYDROXIDE AS ELECTROLYTE

No.	C ₃ H ₈ O	NaOH	Freezing point, °C.	No.	C ₃ H ₈ O	NaOH	Freezing point, °C.
0	—	—	0.000	45	0.666	0.984	-5.462
3	0.660	—	-1.260	10	1.280	0.062	-2.762
9	1.280	—	-2.537	11	1.280	0.142	-3.362
17	1.680	—	-3.434	12	1.280	0.471	-4.802
22	2.390	—	-4.607	46	1.280	0.934	-7.257
1	—	0.154	-0.560	18	1.680	0.060	-3.746
5	—	0.067	-0.361	19	1.680	0.139	-4.179
7	—	0.512	-1.862	20	1.680	0.461	-5.897
6	0.666	0.064	-1.710	49	1.680	0.919	-8.557
4	0.666	0.147	-1.901	23	2.390	0.047	-4.872
28	0.666	0.315	-2.680	24	2.390	0.132	-5.292
27	0.666	0.488	-3.362	25	2.390	0.439	-7.152

TABLE V
WITH POTASSIUM HYDROXIDE AS ELECTROLYTE

No.	C ₃ H ₈ O	NaOH	Freezing point, °C.	No.	C ₃ H ₈ O	NaOH	Freezing point, °C.
63	—	—	0.000	65	0.660	0.304	-2.540
72	—	0.634	-2.292	66	1.280	0.290	-3.955
73	—	0.317	-1.182	67	1.280	0.590	-5.525
64	0.660	0.607	-3.920				

If the concentration of aqueous sodium hydroxide be plotted against specific conductivity, an almost linear relation is obtained over the range here employed. If acetone be substituted for some of this water, there is observed a falling-off in conductivity which varies with the acetone concentration.

A decrease in conductivity may be due to one or more of the following factors:

- (a) Removal of ions from solution;
- (b) An increase in viscosity;
- (c) A decrease in the number of "active" particles through the lowering of the dielectric constant of the solution.

Formula of Lenz (10)

Lenz formulated an equation that predicates that the resistance of a solution of an electrolyte can be calculated by taking into account the volume per cent of non-electrolyte added to displace water from a solution whose conductivity is known. In his equation the constant "*b*" was found from these data to vary irregularly from 0.0166 to 0.0482,—obviously an unsatisfactory relation.

Formula of Stephan (15)

This simple relation applies only to the viscosities and conductivities of the aqueous and the mixed-solvent solutions. With these data in Stephan's equation, the variations, if calculated from the observed, were from +2% to -5% for acetone concentrations as high as 1.78 *M*. For 4.5 *M* acetone the variation was between +18% and -3%.

Formula of Arrhenius (2)

In the publication of his extensive researches into the conductivity of acids, bases and salts in mixed solvents, no data are given for the alkali-acetone-water system. This equation is concerned with the volume per cent of added non-electrolyte (similar to that of Lenz), and is found to hold well for 0.88 *M* or 6.31 volume per cent acetone. Above this, however, the calculated conductivity varies from the observed by from +12% to -6%, the variation increasing with acetone concentration.

Formula of Wakeman (17)

This, like the Lenz and Arrhenius equations, makes use of volume per cent of non-electrolyte replacing water in the solution. The constant calculated varied irregularly from 0.022 to 0.036.

Formula of Cohen (7)

This is a simple relation based on concentration only. Here again the constant varied from 1.10 to 2.57, being lowest with low concentrations and highest with high concentrations of both acetone and sodium hydroxide.

The equations mentioned above show their inapplicability to solutions of high acetone concentration because they consider only one of the factors, concentration and viscosity, at a time.

Significance of the Volume Change

In this work it was found that, besides the regular volume change expected on mixing acetone and water (which was virtually instantaneous), there was always a subsequent additional decrease. This decrease was smaller than the

instantaneous one and much slower in attainment, but became larger as the acetone concentration increased. This time-change was larger still when aqueous sodium hydroxide was used in place of water, and its magnitude increased with alkali concentration, but no direct proportionality was found to exist.

Check experiments with potassium chloride in place of sodium hydroxide showed a similar volume change, but this was not nearly so pronounced.

This volume change may be explained perhaps as the result of a temperature change on mixing, but with sodium hydroxide present this is not so obvious an explanation.

The object in finding the freezing points of mixtures (shown in Tables IV and V) was to determine whether a decrease in solute particles had occurred. Actually none does occur, and since the same is true of potassium as well as of sodium hydroxide, it may be safely assumed that solvation or hydration of the ions is not a significant factor in this instance. Similarly no complex between acetone and alkali results, otherwise the freezing point data would have indicated it. It is possible however that the alkali causes a depolymerization or dissociation of either the acetone or the water. This idea agrees well with the viscosity results (Table II), where the effect on the viscosity of a fixed quantity of alkali increases with the acetone concentration, and the viscosity change is much greater with acetone than with water in the presence of alkali. This is in agreement with the work of Bousfield and Lowry (5) who found that the behavior of water was simpler with increased sodium hydroxide concentration. This depolymerization of the acetone or water aggregates (or both) evolves heat, with subsequent expansion as the sodium hydroxide concentration increases, and this delays the attainment of the final volume. The facts found by Bancroft and Gould (3) in connection with mono- and dihydrol likewise support the above idea.

In spite, therefore, of the initial conductivity being observed while the solution is adjusting itself, the relation between initial and final conductivity is remarkably constant. In all calculations used here it is the final conductivity value that is taken.

Summing up the application of the equations given to the data obtained, it is apparent that with dilute solutions the viscosity relation holds the best. But with higher concentrations of acetone a further factor enters. That the ions might be solvated (with acetone molecules) was tested by passing a direct current through solutions of acetone, water and alkali in various concentrations. Determinations of alkalinity and acetone were made at the electrodes, but there was no noticeable change in acetone concentration.

Enolization of Acetone

The results given by Evans and Nicoll (8) showed that at 0.036 *M* concentration of potassium hydroxide, 26% of the acetone present was enolic, there being no change with further increase of alkali.

This was checked by studying the change in refractive power of acetone-water mixtures with various concentrations of alkali present. Without alkali, these mixtures in volume relations showed values of linear connection as demanded by the mixing rule.

Mixtures were then studied at 21° C. with sodium hydroxide constant at 0.1 *M* concentration. The results obtained (Table VI) do not agree with those of Evans and Nicoll.

Whatever the significance of these results, they do not afford a possible explanation of the conductivity values.

TABLE VI
SPECIFIC REFRACTION AND CONCENTRATION

Vol. % C ₃ H ₆ O	Specific refraction of mixture	Specific refraction of mixture and NaOH	% Diff.	% Enol
50	0.382	0.387	1.3	22.0
40	0.370	0.374	1.1	19.0
25	0.355	0.357	0.56	9.9

Dielectric Relations

Åkerlöf (1) obtained values for the dielectric constants of acetone and water, and showed that the change in value is virtually in direct proportion to the amount of second liquid added.

A study of the reasoning of Nernst (12), Thomson (16), Walden (19), Sachanov (13), Bray and Kraus (6), Walden (18), Smale (14), and Lattey (9) indicated that, though no direct proportionality may exist between dielectric constant and ionizing power, yet there is more than a semblance of such relation in solvents of high, than in those of low, dielectric constant.

By the use of Åkerlöf's figures and extrapolating and applying these to the data found here, values may be obtained from the formula, sp. conductivity of mixture $\times \frac{\text{dielectric constant of water}}{\text{dielectric constant of mixture}}$ is equal to the specific conductivity in water only. The values obtained show little agreement with the observed conductivities, but when they are combined with viscosity the relation

$$C_m = C_w \left\{ \frac{N_w \times D_m}{N_m \times D_w} \right\},$$

is obtained, where N_w and N_m are the viscosities and D_w and D_m are the dielectric constants of water and the mixtures respectively; C_m is the specific conductivity of the mixture and C_w that of sodium hydroxide in water only.

Table VII shows these values and also the ratio C_m (obs.) \div C_m (calc.). Here, in contrast with the equations considered previously, this ratio is always greater than 1, and except for No. 19 the agreement is good, considering that this ratio contains all the experimental errors of volume change, viscosity,

TABLE VII
SPECIFIC CONDUCTIVITY, DIELECTRIC CONSTANT AND VISCOSITY

No.	D_m/D_w	N_w/N_m	C_m calc.	$C_m(\text{obs.})/C_m(\text{calc.})$
17	0.954	0.820	0.0986	1.085
18	0.954	0.855	0.0517	1.071
19	0.954	0.885	0.0258	1.029
20	0.954	0.870	0.0113	1.087
21	0.954	0.855	0.0055	1.094
22	0.913	0.757	0.0046	1.065
23	0.913	0.746	0.0090	1.105
24	0.913	0.730	0.0194	1.098
25	0.913	0.709	0.0389	1.152
26	0.913	0.704	0.0787	1.113
27	0.797	0.470	0.0391	1.064
28	0.797	0.510	0.0203	1.074
29	0.797	0.535	0.0101	1.060
30	0.797	0.555	0.0047	1.058
31	0.797	0.556	0.0024	1.060
				Mean = 1.080

dielectric constant extrapolation and resistance determinations. It may be observed that this ratio is not dependent on the concentration of either alkali or acetone and is somewhat more constant at the higher concentrations—where the other equations hold with least fidelity.

Thus in the absence of any quantitative connections between dielectric constant and ionization this empirical equation is presented

$$C_m = C_w \left\{ \frac{N_w \times D_m}{N_m \times D_w} \right\} \times K$$

where $K = 1.080$.

It is not impossible to justify this equation: sodium hydroxide is a strong electrolyte, and, if the dielectric constant falls off so sharply with addition of acetone, some of the ions will associate to decrease the conductivity. A decrease in dielectric constant will also increase the ionic atmosphere and retard ionic movement,—the latter being accentuated by the sharp viscosity changes in the region of these determinations.

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THE EFFECT OF VARIOUS STARCHES ON THE STABILITY OF BAKING POWDERS¹

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Abstract

A study has been made of the stabilizing effect of potato, corn, wheat and rice starches in phosphate, tartrate and combination baking powders under widely differing conditions of storage. The stabilizing effect was found to depend on the size of the starch granule, decreasing efficiency being obtained with increasing granular size in the following order: rice, wheat, corn, potato. Microscopic observations were made to determine the physical effect of the starch. Small wheat granules were found to be more efficient than large ones, and finely powdered wheat starch more efficient than coarse wheat starch. The stability is greater with increasing particle size of acid constituent, and the crystal form of the latter is also important. The difference in stability lent by the various starches is increasingly accentuated with increasing fineness of acid constituent. The stability decreases rapidly with rise in relative humidity. The moisture take-up of potato, corn and wheat starches at different humidities has been measured.

Baking powders, with the exception of several recently proposed (2), consist of sodium bicarbonate, an acid constituent and a starch. The classification of baking powders depends on the acid constituent employed, and three general types are at present in use in Canada and the United States: phosphate powders, containing monocalcium phosphate or sodium acid pyrophosphate, usually the former; tartrate powders, containing potassium bitartrate with or without tartaric acid; combination powders, containing S.A.S. (sodium aluminium sulphate) and monocalcium phosphate. Leavening occurs as a result of the expansion of the carbon dioxide formed by the interaction of the acidic and basic constituents of the baking powder in the moist dough or batter, and the "strength" of the baking powder, *i.e.*, the amount of carbon dioxide produced per unit weight, must be reasonably constant to obtain optimum results. Baking powders for household use are, on the average, made up to contain about 14%, and commercial powders about 17%, of total carbon dioxide.

The acidic and basic components alone react comparatively quickly in the presence of atmospheric humidity and a stabilizing diluent, generally corn starch, is added to the mixture. The stabilizing effect has been ascribed to either or both of the following factors, (i) the preferential take-up of moisture by the starch, (ii) the mechanical effect of physically separating the acidic and basic constituents. The baking powder is stored both before reaching the consumer and during use, and the keeping quality is an important property of the material.

¹ Manuscript received May 9, 1936.

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The effect of temperature on the stability of baking powders is of lesser practical importance since the temperature of storage generally should not rise greatly above prevailing summer temperatures, and this factor has not been considered in the present work. The relative humidity during preservation may, however, vary over almost the whole possible range, and this factor has been particularly investigated. The type of starch used, and the fineness of subdivision of the ingredients of the baking powder have been found important factors in the stability.

Results

The tables given in the experimental section show the results obtained on testing the stability of various baking powders made up with different starches and under varying conditions of preservation. Other factors being the same, the stability increases with increasing size of acid phosphate. However, it is found in use that granular size greater than a certain maximum (in the region of 100 mesh) results in local concentration of acid with the consequent formation of black spots in the baked product. The granular size of acid phosphate used in practice is consequently a compromise between these two factors. In the present work there have been included powdered acid phosphate and two types of granular acid phosphates of different mesh sizes.

It is noted that in the powdered phosphate baking powders, rice starch lends the greatest stability, followed by corn, coarse wheat and potato starches in order of decreasing stability. The relation at 77% relative humidity shows very large differences in effect. Exposure to this humidity, which is greater than that normally encountered in practice, may be regarded as an accelerated stability test. With decreasing relative humidity, the differences become less, until at 33% all the powders still contained more than 12% total carbon dioxide after four months continuous exposure. Storage in tightly stoppered flasks and in tins, with short exposures each day, showed the same order of stabilizing efficiency in the starches. The latter condition of exposure simulates somewhat conditions in household use. The tartrate and combination powders showed the same order of stability with respect to the starches, and the granular phosphate powders the same order for corn and potato starches.

For proper comparison, the wheat starch generally used in these experiments, somewhat coarser than the other starches, was ground to a comparable degree of fineness. It was found that this finely ground wheat starch was much superior to the coarser wheat starch as a baking powder stabilizer. Furthermore this properly ground wheat starch is superior to corn starch in stabilizing efficiency.

Since wheat starch consists of granules of two quite distinct sizes, a separation was effected and the larger and smaller granules tested separately. The superiority of the small granules in stabilizing effect was very marked. Some of the results obtained are shown in Fig. 1, similar results being obtained in other cases.

up with varying mesh size of acid calcium phosphate. In the tartrate powders, in which the acid constituents are of the granular type, although the order of merit of the starches in lending stability remains the same, the differences among the starches are much smaller than those found for the powders containing finely divided acid constituents, and become unimportant at lower humidities. Intermittent exposure for five minutes per day to the laboratory atmosphere showed practically no difference in effect among the starches in the tartrate and combination baking powders over long periods of preservation.

The effect of relative humidity on the stability is very marked in all the baking powders, the instability increasing greatly at relative humidities greater than 40%.

Measurements were made also of the comparative moisture take-up of various starches at different humidities (Table XIX). The differences obtained do not appear to be sufficiently great to be an important factor in the relative stability lent by these starches to baking powders.

General

Experimental

The starches used were dried overnight at 50° C., the moisture content being brought down to 4-5%. In the preparation of the baking powders, the acid constituent was thoroughly mixed with a portion of the starch to be used, and the sodium bicarbonate with the remainder of the starch, after which the whole was thoroughly mixed together. Accurately weighed samples (about 0.8 gm.) of the baking powder were placed in small cones of folded high-grade filter paper, which were then exposed to standard humidities in desiccators at room temperature. These relative humidities were maintained by the use of saturated solutions of inorganic salts. In other experiments, the baking powders were preserved in tins (set-in lid) and exposed for five minutes each day to the prevailing laboratory atmosphere, with shaking before each exposure. The type of tin and the height of solid in the tin were the same in all cases. In another series, the baking powders were preserved in tightly stoppered glass vessels, the volume of air in each being approximately the same.

The measurement of total carbon dioxide in the sample was carried out volumetrically in the Chittick apparatus (1). Ten cubic centimetres of 1 : 4 sulphuric acid was used to liberate the carbon dioxide in each sample, and mercury was used as a leveling liquid in place of the liquid recommended (1).

After the usual pressure and temperature corrections, the weight of carbon dioxide, weight per cent of carbon dioxide and loss of carbon dioxide in percentage of the amount contained in the original material were calculated. Two errors enter into this measurement, *viz.*, the carbon dioxide that dissolves in the acid solution and the aqueous tension of the added liquid. A series of preliminary determinations on known weights of sodium bicarbonates gave results almost identical with theory, and it was assumed that these errors are, practically speaking, equal in magnitude and cancel each other.

Experimental errors, as noted in some irregular deviations in the tables, are probably due rather to unavoidable differences in the tightness of packing in the cones or tins and in the consequent differences in ease of access of moisture to the samples. The preservations were not made at a standard temperature, and the variation in laboratory temperature would cause a slight variation in results.

The fineness of division of the sodium bicarbonate and of all acidic constituents was held standard in all the experiments, similarly also in the case of potato, corn and rice starches. The wheat starch generally used in these experiments was coarser than the other starches, and in several series finely ground wheat starch was used. Through the courtesy of Dr. H. D. Chataway, there were obtained separated samples of small and large wheat starch granules, separated by her in an air-flotation apparatus.

Unless otherwise stated, "wheat" refers to the coarser wheat starch generally used in these experiments.

Phosphate

Approximate composition:—sodium bicarbonate, 26.7; starch, 39.9; mono-calcium phosphate, 33.4%.

TABLE I
STABILITY OF POWDERED PHOSPHATE BAKING POWDER AT 77% RELATIVE HUMIDITY

No. days exposed	Volume CO ₂ , cc.				Weight % CO ₂				% Loss of CO ₂			
	Potato	Corn	Wheat	Rice	Potato	Corn	Wheat	Rice	Potato	Corn	Wheat	Rice
0	68.9	66.7	67.7	66.8	14.8	14.0	14.3	14.0	0	0	0	0
0.34	45.2	62.4	51.0	65.0	9.5	13.2	11.0	13.9	35.8	5.7	23.1	0.7
0.34	44.5	63.1	51.4	—	9.5	13.1	11.0	—	35.8	6.4	23.1	—
1	28.6	55.0	33.9	56.0	6.1	11.4	7.2	12.2	58.8	18.6	49.6	12.9
2	19.7	38.0	30.9	45.6	4.3	8.2	6.6	9.7	70.9	41.4	53.9	30.7
4	12.2	22.2	28.7	33.2	2.6	4.8	5.6	7.3	82.4	65.7	60.8	47.9
6	—	—	—	21.6	—	—	—	4.6	—	—	—	67.1
7	13.6	25.6	27.2	—	2.8	5.4	5.8	—	81.1	61.4	59.5	—
10	—	—	—	18.9	—	—	—	4.0	—	—	—	71.5

TABLE II
EFFECT OF FINENESS OF GRINDING OF WHEAT STARCH ON THE STABILIZATION OF POWDERED PHOSPHATE BAKING POWDER—RELATIVE HUMIDITY, 77%

No. days exposed	Vol. CO ₂ , cc.		Wt. % CO ₂		% Loss CO ₂	
	Coarse	Fine	Coarse	Fine	Coarse	Fine
0	67.7	64.0	14.3	13.6	0	0
0.34	51.0	57.3	11.0	12.3	23.1	9.5
1	33.9	48.4	7.2	10.6	49.6	22.0
2	30.9	38.8	6.6	8.4	53.9	38.2
4	28.7	34.8	5.6	7.6	60.8	44.1
7	27.2	22.0	5.8	4.8	59.5	64.7
10	—	19.2	—	4.2	—	69.1

TABLE III
EFFECT OF GRANULAR SIZE OF WHEAT STARCH ON THE STABILIZATION OF POWDERED
PHOSPHATE BAKING POWDER—RELATIVE HUMIDITY, 77%

No. days exposed	Vol. CO ₂ , cc.		Wt. % CO ₂		% Loss CO ₂	
	Small*	Large	Small	Large	Small	Large
0	35.0	58.4	14.3	12.6	0	0
0.79	35.9	—	12.2	—	14.7	—
1	—	36.8	—	7.9	—	37.3
1.79	36.8	—	12.1	—	15.4	—
2	—	27.4	—	5.7	—	54.8
3	—	21.3	—	4.6	—	63.5
3.79	29.4	—	9.8	—	31.5	—
5	—	14.9	—	3.1	—	75.4
5.79	20.2	—	7.0	—	51.0	—
8	—	11.3	—	2.4	—	81.0
8.75	17.9	—	5.7	—	60.2	—

* Smaller samples used—0.4 to 0.55 gm.

TABLE IV
STABILITY OF POWDERED PHOSPHATE BAKING POWDER AT 60% RELATIVE HUMIDITY

No. days exposed	Vol. CO ₂ , cc.			Wt. % CO ₂			% Loss CO ₂		
	Potato	Corn	Wheat	Potato	Corn	Wheat	Potato	Corn	Wheat
0	67.0	65.0	64.2	13.9	13.8	13.8	0	0	0
1	51.4	60.0	62.8	11.0	13.0	13.4	20.9	5.8	2.9
3	46.8	64.2	45.0	9.8	12.9	9.5	29.5	6.5	31.2
7	47.0	58.6	42.6	9.5	12.3	9.0	31.7	10.9	34.8
13	42.6	58.8	41.0	8.7	12.3	8.5	37.4	10.9	38.4
24	41.4	—	—	8.9	—	—	36.0	—	—
29	43.2	55.2	39.0	8.8	12.0	8.2	36.7	13.1	40.6

TABLE V
STABILITY OF POWDERED PHOSPHATE BAKING POWDER AT 55% RELATIVE HUMIDITY

No. days exposed	Volume CO ₂ , cc.				Weight % CO ₂				% Loss of CO ₂			
	Potato	Corn	Wheat	Rice	Potato	Corn	Wheat	Rice	Potato	Corn	Wheat	Rice
0	67.0	65.0	64.2	66.8	13.9	13.8	13.8	14.0	0	0	0	0
1	56.4	61.3	60.6	64.2	11.8	13.2	13.1	13.4	15.1	4.3	5.1	4.3
3	54.3	60.6	48.6	—	11.1	12.7	10.1	—	20.1	8.0	26.8	—
6	—	—	—	60.4	—	—	—	13.1	—	—	—	6.4
7	49.8	60.3	43.2	—	10.4	12.6	9.1	—	25.2	8.7	34.0	—
13	49.8	59.4	43.2	61.0	10.5	12.5	8.7	13.4	24.5	9.4	37.0	4.3
24	46.8	59.4	40.8	—	10.0	12.3	8.3	—	28.1	10.9	39.9	—
27	—	—	—	60.4	—	—	—	13.1	—	—	—	6.4
39	44.6	—	40.2	—	9.4	—	8.3	—	32.4	—	39.9	—
41	—	—	—	62.5	—	—	—	13.5	—	—	—	3.6
64	—	—	—	64.8	—	—	—	13.2	—	—	—	5.7

TABLE VI
EFFECT OF FINENESS OF GRINDING OF WHEAT STARCH ON THE STABILIZATION OF POWDERED
PHOSPHATE BAKING POWDER—RELATIVE HUMIDITY, 55%

No. days exposed	Vol. CO ₂ , cc.		Wt. % CO ₂		% Loss CO ₂	
	Coarse	Fine	Coarse	Fine	Coarse	Fine
0	64.2	60.7	13.8	13.3	0	0
1	60.6	57.0	13.1	12.7	5.1	4.5
3	48.6	57.0	10.1	12.4	26.8	6.8
7	43.2	—	9.1	—	34.0	—
8	—	56.5	—	12.5	—	6.0
10	—	56.6	—	12.3	—	7.5
11.88	—	56.0	—	12.2	—	8.3
13	43.2	—	8.7	—	37.0	—

TABLE VII
STABILITY OF POWDERED PHOSPHATE BAKING POWDER AT 33% RELATIVE HUMIDITY

No. days exposed	Volume CO ₂ , cc.				Weight % CO ₂				% Loss of CO ₂			
	Potato	Corn	Wheat	Rice	Potato	Corn	Wheat	Rice	Potato	Corn	Wheat	Rice
0	67.0	65.0	64.2	66.8	13.9	13.8	13.8	14.0	0	0	0	0
1	66.4	63.6	64.0	—	13.4	13.7	13.7	—	3.6	0.7	0.7	—
2	—	—	—	66.2	—	—	—	14.0	—	—	—	0
6	67.0	64.0	66.0	—	14.0	13.5	13.8	—	0	2.2	0	—
13	62.7	65.2	66.2	61.2	13.4	13.8	14.0	13.5	3.6	0	0	3.6
25	59.2	64.6	64.8	—	12.8	13.4	13.9	—	7.9	2.9	0	—
39	60.0	64.2	62.4	—	12.5	13.3	13.3	—	10.0	3.6	3.6	—
41	—	—	—	65.0	—	—	—	13.8	—	—	—	1.4
76	56.4	58.5	58.8	—	12.4	12.6	13.1	—	10.8	8.7	5.1	—
121	—	—	—	64.4	—	—	—	14.0	—	—	—	0

TABLE VIII
STABILITY OF POWDERED PHOSPHATE BAKING POWDER IN TINS EXPOSED 5 MIN. PER 24 HR.

No. days preserved	Vol. CO ₂ , cc.			Wt. % CO ₂			% Loss CO ₂		
	Potato	Corn	Wheat	Potato	Corn	Wheat	Potato	Corn	Wheat
0	62.8	65.2	63.8	13.5	14.0	13.6	0	0	0
7	66.8	67.0	61.8	13.8	14.1	13.2	0	0	2.9
15	61.8	66.0	63.2	12.6	13.6	13.1	6.7	2.9	3.7
24	61.0	64.4	58.8	12.8	13.8	12.6	5.2	1.4	7.3
33	60.4	64.3	63.2	12.8	13.4	13.0	5.2	4.3	4.4
49	54.7	59.3	58.0	11.8	12.8	12.2	12.6	8.6	10.3
70	33.5	59.0	41.1	7.4	13.0	9.2	45.2	7.1	32.3
70	34.9	—	—	7.5	—	—	44.4	—	—
87	36.6	58.4	36.1	7.9	12.6	7.7	40.0	10.0	43.4
125	29.9	50.8	30.4	6.8	11.5	6.9	57.0	17.8	49.3

TABLE IX
STABILITY OF POWDERED PHOSPHATE BAKING POWDER IN STOPPERED FLASKS

No. days preserved	Vol. CO ₂ , cc.			Wt. % CO ₂			% Loss CO ₂		
	Potato	Corn	Wheat	Potato	Corn	Wheat	Potato	Corn	Wheat
0	68.9	66.7	67.7	14.8	14.0	14.3	0	0	0
2.5	63.0	65.4	67.1	13.5	13.6	13.6	8.8	2.9	4.9
4.5	64.6	63.4	64.3	13.6	13.7	13.7	8.1	2.1	4.2
7.5	63.0	63.9	63.1	13.3	13.6	13.4	10.1	2.9	6.3
31	64.2	63.4	63.4	13.7	13.7	13.7	7.4	2.1	4.2

TABLE X
STABILITY OF GRANULAR PHOSPHATE BAKING POWDER AT 77% RELATIVE HUMIDITY

Mesh	No. days exposed	Vol. CO ₂ , cc.		Wt. % CO ₂		% Loss of CO ₂	
		Potato	Corn	Potato	Corn	Potato	Corn
(a) Monocalcium Phosphate "A"							
+100	0	62.8	64.2	13.6	13.9	0	0
	1	61.2	62.1	13.2	13.4	2.9	3.6
	2	57.6	59.5	12.4	12.8	8.8	7.9
	4	53.2	58.5	11.5	12.7	15.4	8.6
	7	44.8	50.7	9.9	11.2	27.2	15.8
	10	38.2	45.2	8.1	9.5	40.4	31.7
-100	0	63.2	64.0	13.7	13.8	0	0
	1	57.0	60.0	12.3	12.9	10.2	6.5
	2	51.7	56.8	11.1	12.6	19.0	8.7
	4	39.3	56.6	7.5	12.3	45.2	10.9
	7	32.2	44.0	7.1	9.7	48.2	29.7
	10	26.4	38.0	5.6	8.1	59.1	41.3
+150	0	64.4	64.0	13.9	13.8	0	0
	1	49.8	56.8	10.8	12.3	22.3	10.9
	2	44.2	53.2	9.5	11.4	31.7	17.4
	4	28.8	47.8	6.2	10.4	55.4	24.6
	7	24.5	37.8	5.4	8.1	61.2	41.3
	10	21.0	28.1	4.5	6.0	67.6	56.5
-150	0	64.4	64.0	13.9	13.8	0	0
	1	49.8	56.8	10.8	12.3	22.3	10.9
	2	44.2	53.2	9.5	11.4	31.7	17.4
	4	28.8	47.8	6.2	10.4	55.4	24.6
	7	24.5	37.8	5.4	8.1	61.2	41.3
	10	21.0	28.1	4.5	6.0	67.6	56.5
+200	0	62.8	65.2	13.6	14.1	0	0
	1	33.0	56.4	7.1	12.1	47.8	14.2
	2	22.0	47.0	4.7	10.1	65.4	28.4
	4	19.8	44.6	4.3	9.7	68.4	31.2
	7	20.0	23.5	4.4	5.2	67.6	63.1
	10	—	19.0	—	4.1	—	70.9
(b) Monocalcium Phosphate "B"							
+100	0	60.4	64.5	13.3	14.1	0	0
	1	53.0	59.5	11.7	12.8	12.0	9.2
	2	51.4	53.4	10.2	11.7	22.5	17.0
	4	46.4	47.2	9.8	10.4	26.3	26.2
	7	34.0	33.2	7.4	7.3	44.3	48.2
	10	28.0	27.8	6.0	6.0	55.0	57.4
-100	0	60.0	64.8	13.1	14.2	0	0
	1	54.4	61.2	11.7	13.1	10.7	7.7
	2	52.6	56.0	11.4	12.3	13.0	13.4
	4	46.4	49.8	10.1	11.0	22.9	22.5
	7	33.2	29.0	7.2	6.3	45.0	55.6
	10	26.1	25.0	5.6	5.4	57.0	62.0
+150	0	60.0	64.8	13.1	14.2	0	0
	1	54.4	61.2	11.7	13.1	10.7	7.7
	2	52.6	56.0	11.4	12.3	13.0	13.4
	4	46.4	49.8	10.1	11.0	22.9	22.5
	7	33.2	29.0	7.2	6.3	45.0	55.6
	10	26.1	25.0	5.6	5.4	57.0	62.0
-150	0	61.9	64.6	13.5	14.0	0	0
	1	52.0	59.1	11.2	12.8	17.0	8.6
	2	36.0	53.1	7.8	11.4	42.2	18.6
	4	31.2	39.2	6.8	8.5	49.6	39.3
	7	22.4	28.6	4.9	6.3	63.7	55.0
	10	19.2	21.4	4.1	4.6	69.6	67.1
+200	0	60.8	64.4	13.3	13.9	0	0
	1	49.2	54.6	10.6	11.8	20.3	15.1
	2	28.6	42.6	6.2	9.2	53.4	33.8
	4	26.2	31.6	5.7	6.8	57.1	51.1
	7	21.2	25.8	4.6	5.7	65.4	59.0
	10	20.0	21.4	4.3	4.6	67.6	66.9
-200	0	60.8	64.4	13.3	13.9	0	0
	1	49.2	54.6	10.6	11.8	20.3	15.1
	2	28.6	42.6	6.2	9.2	53.4	33.8
	4	26.2	31.6	5.7	6.8	57.1	51.1
	7	21.2	25.8	4.6	5.7	65.4	59.0
	10	20.0	21.4	4.3	4.6	67.6	66.9

Tartrate

Approximate composition:—sodium bicarbonate, 26.7; starch, 22.4; tartaric acid, 6.0; potassium bitartrate, 44.9%.

TABLE XI
STABILITY OF TARTRATE BAKING POWDER AT 77% RELATIVE HUMIDITY

No. days exposed	Volume CO ₂ , cc.				Weight % CO ₂				% Loss of CO ₂			
	Potato	Corn	Wheat	Rice	Potato	Corn	Wheat	Rice	Potato	Corn	Wheat	Rice
0	68.4	68.2	65.2	64.6	13.9	13.7	13.8	14.1	0	0	0	0
0.25	54.2	60.4	55.4	—	11.4	12.1	11.4	—	18.1	11.7	17.4	—
1	49.6	45.3	45.6	51.6	10.4	9.6	9.7	11.1	25.2	30.0	29.7	21.3
1.88	—	—	—	47.8	—	—	—	10.4	—	—	—	26.2
2	46.7	44.9	44.6	—	9.6	9.3	9.4	—	30.9	32.1	31.9	—
3	45.0	42.7	43.4	—	9.7	9.1	9.4	—	30.2	33.6	31.9	—
7	41.0	44.0	41.5	—	8.9	9.1	8.8	—	36.0	33.6	36.2	—
8	—	—	—	46.8	—	—	—	10.4	—	—	—	26.2
10	—	—	—	46.6	—	—	—	10.2	—	—	—	27.7
11.88	—	—	—	44.7	—	—	—	9.7	—	—	—	31.2

TABLE XII
EFFECT OF FINENESS OF GRINDING OF WHEAT STARCH ON THE STABILIZATION OF TARTRATE BAKING POWDER—RELATIVE HUMIDITY, 77%

No. days exposed	Vol. CO ₂ , cc.		Wt. % CO ₂		% Loss CO ₂	
	Coarse	Fine	Coarse	Fine	Coarse	Fine
0	65.2	63.2	13.8	13.9	0	0
0.25	55.4	—	11.4	—	17.4	—
1	45.6	52.0	9.7	11.6	29.7	16.5
2	44.6	—	9.4	—	31.9	—
3	43.4	49.6	9.4	10.8	31.9	22.3
4.88	—	48.1	—	10.5	—	24.5
7	41.5	—	8.8	—	36.2	—
8	—	46.0	—	10.2	—	26.6
11.88	—	44.6	—	9.7	—	30.2

TABLE XIII
STABILITY OF TARTRATE BAKING POWDER AT 55% RELATIVE HUMIDITY

No. days exposed	Vol. CO ₂ , cc.			Wt. % CO ₂			% Loss CO ₂		
	Potato	Corn	Wheat	Potato	Corn	Wheat	Potato	Corn	Wheat
0	68.4	68.2	65.2	13.9	13.7	13.8	0	0	0
1	62.5	63.6	62.8	13.2	13.6	13.4	5.0	0.7	2.9
3	56.5	62.6	57.8	12.2	12.8	12.5	12.2	6.5	9.4
7	54.5	58.4	55.0	11.4	12.2	11.5	18.0	11.0	16.7
14	51.9	50.2	53.6	11.4	11.0	11.5	18.0	19.7	16.7
28	52.0	50.0	50.6	11.3	10.9	10.9	18.7	20.4	21.0

TABLE XIV
STABILITY OF TARTRATE BAKING POWDER AT 33% RELATIVE HUMIDITY

No. days exposed	Vol. CO ₂ , cc.			Wt. % CO ₂			% Loss CO ₂		
	Potato	Corn	Wheat	Potato	Corn	Wheat	Potato	Corn	Wheat
0	68.4	68.2	65.2	13.9	13.7	13.8	0	0	0
1	65.4	63.8	65.6	13.7	13.1	13.6	1.4	4.4	1.4
7	63.8	63.2	62.6	13.0	13.1	13.2	6.5	4.4	4.3
14	60.8	60.4	60.6	13.4	13.2	13.4	3.6	3.6	2.9
28	58.1	61.2	62.4	12.5	13.4	13.6	10.0	2.2	1.4
56	65.0	65.3	64.6	13.4	13.7	13.5	3.6	0	2.2

TABLE XV
STABILITY OF TARTRATE BAKING POWDER IN TINS EXPOSED 5 MIN. PER 24 HR.

No. days preserved	Vol. CO ₂ , cc.			Wt. % CO ₂			% Loss CO ₂		
	Potato	Corn	Wheat	Potato	Corn	Wheat	Potato	Corn	Wheat
0	68.4	68.2	65.2	13.9	13.7	13.8	0	0	0
7	63.4	64.0	63.2	13.3	13.3	13.2	4.3	2.9	4.3
14	58.5	62.3	61.8	12.9	13.3	13.3	7.2	2.9	3.6
28	60.3	61.1	59.4	13.1	13.1	12.9	5.8	4.3	6.5
46	59.5	61.8	63.4	12.8	13.1	13.0	7.9	4.3	5.8
79	59.3	57.6	57.6	13.4	13.0	13.0	3.6	5.1	5.8
120	56.7	57.5	57.3	12.5	12.7	12.7	10.1	8.0	8.0

Combination (S.A.S. Phosphate)

Approximate composition:—sodium bicarbonate, 28.0; starch, 42.0; sodium aluminium sulphate, 17.0; monocalcium phosphate, 13.0%.

TABLE XVI
STABILITY OF S.A.S.—POWDERED PHOSPHATE BAKING POWDER AT 77% RELATIVE HUMIDITY

No. days exposed	Vol. CO ₂ , cc.			Wt. % CO ₂			% Loss CO ₂		
	Potato	Corn	Rice	Potato	Corn	Rice	Potato	Corn	Rice
0	67.0	66.3	67.2	14.5	14.3	14.9	0	0	0
0.25	66.0	66.9	—	13.8	14.3	—	4.8	0	—
1	54.1	60.6	65.2	11.5	13.0	14.5	20.7	9.1	2.7
3	46.7	53.6	61.0	10.3	11.5	13.3	29.0	19.6	10.7
5	42.8	47.6	—	9.5	10.5	—	34.5	26.6	—
8	42.1	45.2	48.3	8.9	9.7	10.7	38.6	32.2	28.2
10	—	—	44.7	—	—	9.7	—	—	34.9
11.88	—	—	42.3	—	—	9.2	—	—	38.2
12	40.5	42.4	—	8.8	9.2	—	39.3	35.7	—

TABLE XVII

STABILITY OF S.A.S.—POWDERED PHOSPHATE BAKING POWDER IN TINS EXPOSED
5 MIN. PER 24 HR.

No. days preserved	Vol. CO ₂ , cc.		Wt. % CO ₂		% Loss CO ₂	
	Potato	Corn	Potato	Corn	Potato	Corn
0	67.0	66.3	14.5	14.3	0	0
8	66.5	68.4	14.2	14.4	2.1	0
49	65.4	61.5	14.8	13.9	2.1	—
90	62.2	63.0	13.7	13.8	5.8	3.5

TABLE XVIII

STABILITY OF S.A.S.—GRANULAR PHOSPHATE BAKING POWDER AT 77% RELATIVE HUMIDITY
(Monocalcium phosphate "A")

Mesh	No. days exposed	Vol. CO ₂ , cc.		Wt. % CO ₂		% Loss CO ₂	
		Potato	Corn	Potato	Corn	Potato	Corn
+100	0	67.0	67.0	14.5	14.5	0	0
	1	61.2	63.0	13.3	13.7	8.3	5.3
	2	58.6	60.4	12.8	13.2	11.7	9.0
	4	53.0	59.2	11.6	12.9	20.0	11.0
	7	49.6	57.0	10.9	12.6	24.8	13.1
	10	47.0	54.8	10.3	12.0	29.0	17.3
-100 +150	0	66.8	67.2	14.5	14.6	0	0
	1	60.0	62.2	13.0	13.5	10.3	7.5
	2	56.0	60.6	12.2	13.2	15.9	9.7
	4	51.1	58.2	11.1	12.7	23.4	13.0
	7	46.7	55.4	10.3	12.2	29.0	16.4
	10	44.2	52.4	9.6	11.5	33.8	21.2
-150 +200	0	67.0	68.0	14.5	14.7	0	0
	1	58.4	61.6	12.7	13.4	12.4	8.8
	2	53.1	59.2	11.6	12.9	20.0	12.2
	4	49.4	56.8	10.8	12.4	25.5	15.6
	7	44.4	53.0	9.8	11.7	32.4	20.4
	10	41.0	49.6	9.0	10.8	38.0	26.5
-200	0	68.0	67.4	14.7	14.6	0	0
	1	54.2	59.6	11.8	12.9	19.7	11.6
	2	48.6	58.0	10.6	12.6	27.9	13.7
	4	44.6	53.2	9.7	11.6	34.0	20.5
	7	40.6	47.2	9.0	10.4	38.8	28.7
	10	39.2	44.0	8.5	9.6	42.2	34.3

Moisture Take-up

The starches were dried at 105° C. for several hours and the weight taken as the zero moisture weight. Exposures were then made in desiccators to standard humidities, and the increase in weight was noted.

TABLE XIX
MOISTURE TAKE-UP OF STARCHES

Starch	% Water after exposure for following periods							
I. 77% Relative humidity								
	0 hr.	6 hr.	24 hr.	48 hr.	72 hr.	96 hr.	122 hr.	
Potato	0	2.87	7.83	10.27	11.35	11.95	12.20	
Corn	0	2.97	7.15	8.70	9.20	9.46	9.52	
Wheat	0	2.92	6.92	8.52	9.04	9.32	9.42	
II. 55% Relative humidity								
	0 day	1 day	2 days	3 days	5 days	7 days	12 days	21 days
Potato	0	5.5	8.15	9.18	9.73	9.89	10.10	10.11
Corn	0	5.5	7.30	8.03	8.46	8.60	8.77	8.78
Wheat	0	5.0	7.06	7.81	8.16	8.28	8.40	8.39
III. 33% Relative humidity								
	0 day	1 day	2 days	3 days	7 days	13 days	21 days	
Potato	0	3.50	5.14	5.89	6.37	6.53	6.57	
Corn	0	3.61	5.07	5.58	5.88	6.02	6.01	
Wheat	0	3.64	5.07	5.56	5.85	5.91	5.92	

NOTE:—Figures in the last vertical column represent equilibrium values.

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THE SEMI-MICROCOMBUSTION METHOD FOR THE DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS¹

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Abstract

A description is given of a semi-microcombustion method for the estimation of nitrogen in organic compounds. The method is generally applicable and has been uniformly successful. The apparatus and procedure are a combination and simplified modification of several of those previously described in scattered publications.

The published methods for the quantitative estimation of nitrogen in organic compounds on a semi-micro scale have not always given satisfactory or reliable results in this laboratory. Owing to its simplicity, the Kjeldahl method was preferentially employed, but its non-applicability to many classes of substances led the writers to abandon it on account of its unreliability. With a known substance the method could be adjusted so that check results could be obtained, and it undoubtedly has its use, once a standardized procedure can be adopted for specific compounds. Even with its later modifications, where a preliminary reduction by red phosphorus and hydriodic acid is performed (3, 7), one hesitates to accept the results when dealing with unknown substances. Thus, acetylacetone gives a 2,4-dinitrophenylhydrazone, that, by the modified Kjeldahl method, shows 18.6, 18.8% nitrogen (1), which is in the neighborhood of the calculated value (19.0%); a di-dinitrophenylhydrazone would have 23.6% nitrogen. Application of the Dumas method, however, gave the values 23.4, 23.5%, which shows it must be the di-derivative. Since other similar instances were encountered, the use of the Kjeldahl method was abandoned, except for oximes, amines, amides, and such simple substances, and attention was turned to the Dumas method.

The principal cause of trouble with the latter proved to be the source of carbon dioxide. No specimens of natural carbonates available gave, on treatment with acid in the usual manner, carbon dioxide free from inert, insoluble gas, thus making a blank determination necessary and introducing an error. Pure carbon dioxide was eventually obtained by heating sodium bicarbonate, as suggested by Poth (6); the amount of inert gas was negligible and a blank unnecessary. Other authors have advocated the use of magnesite (2,4).

With slight modifications in Lauer's procedure (5), in particular the use of a graduated nitrometer and with small alterations in details of the generator for carbon dioxide, the quantitative estimation of nitrogen became so easily performed and gave such good results without loss of time to acquire a technique, that it seemed advisable to make the observations available to others.

¹ Original manuscript received March 10, 1936.

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1. *The Carbon Dioxide Generator (Fig. 1.)*

This is constructed entirely of Pyrex glass along the general lines suggested by Poth, but with certain changes. Bulbs *S* and *T* are made from 500-cc. flasks, connected by large diameter (2.5 cm.) tubing, and supported by split iron rings, the whole being supported on corks in a tray of sufficient size to collect the mercury in case of accidental breakage. Tube *P* (100 by 3 cm.)

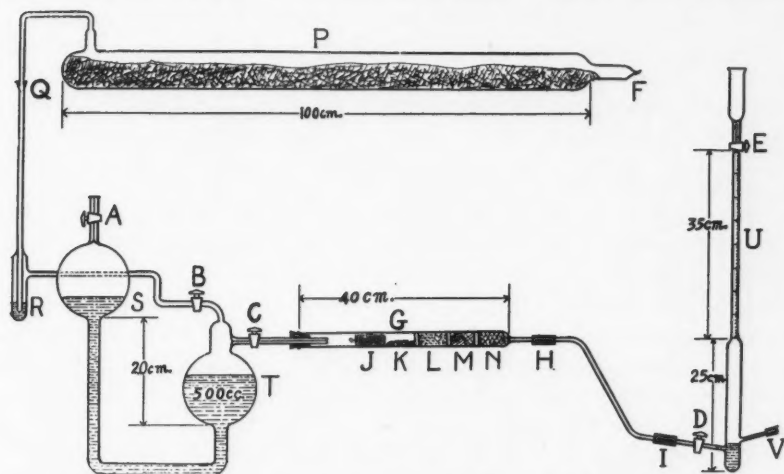


FIG. 1. *Apparatus for semi-micro Dumas method.*

is nearly filled with c.p. sodium bicarbonate, care being taken to leave a free space above it along the length of the tube, and sealed off at *F*. The chief difference between this apparatus and Poth's is the introduction of a stopcock at *B* and a gas-tight ground glass joint at *Q*; these changes obviate the necessity of placing of *P* 100 cm. above *T*, and cutting and resealing the tube when it is necessary to recharge *P*. *R* is a trap to catch any mercury that might get back through *B*. Stopcocks *A* and *C* are of capillary tubing. About 15 lb. of mercury is required to fill the apparatus; when *T* is full, the connecting tube just below *S* should be nearly full. For the refilling of *P*, it is opened at *F*, the sodium carbonate dissolved in warm water and dilute acid, and the tube dried, refilled and sealed.

2. *The Nitrometer, U*

This is constructed from a 10 cc. soft glass gas burette, so graduated that the volume of gas may be read to 0.01 cc. Stopcock *E* is of capillary tubing, but *D* is of ordinary size. A leveling bottle filled with a 50% aqueous potassium hydroxide solution is attached at *V*. The mercury surface at the foot of the nitrometer is "dirtied" by introducing a little finely ground copper

oxide; otherwise bubbles of gas may adhere and introduce an error. The burette is graduated from the stopcock downward, and is calibrated with mercury.

3. *The Combustion Tube, G*

This is constructed of Pyrex, 40–45 cm. long and 1.3 cm. inside diameter, with a sealed-on capillary at the delivery end. Tube *HI* is of capillary size; the connector *H* should be renewed frequently to avoid leakage. A shield of asbestos paper protects it from the heat of the burner. The tube is supported on $\frac{3}{4}$ in. angle iron and heated by three Tirrell burners with wing tops; a large gas flame is essential—ordinary burners do not admit enough gas. The tube is packed in sections as follows, starting at the capillary end, each section being separated by a plug of asbestos to prevent mixing during subsequent handling: a plug of asbestos; 6 cm. of coarse copper oxide, *N*; a 6 cm. roll of copper gauze, *M*; 8 cm. of fine copper oxide, *L*. The sample is mixed with fine copper oxide and a sufficient quantity inserted through a funnel tube to occupy 5 cm. on the bottom of the tube at *K*; *J* is an 8 cm. roll of oxidized copper gauze; this leaves about 6 cm. free space between *J* and the stopper.

4. *Generation of Carbon Dioxide*

A, *B*, and *C* are opened and suction applied at *A*; when the mercury has completely filled *S*, *A* is closed. The pump is then disconnected, and attached at *C*. The level of the mercury will fall in *S* and rise in *T*. The tube *P* is now heated very slightly and the suction continued until the interior pressure is reduced to 2–3 mm.; *C* is closed while *P* is still warm and the pump is disconnected. *P* is now heated gently with a wing-top burner; as gas is evolved the mercury level in *T* will fall. As this occurs, *A* is opened cautiously until the pressures are balanced, and then left open. The heating is continued until a bulb full of gas has been collected, *B* being closed just as the mercury level in *T* starts to rise. A bulb of carbon dioxide usually suffices for three determinations.

To test the carbon dioxide for the presence of inert gas, *C* and *D* are connected by rubber tubing of small bore; *D* is closed and the leveling bulb at *V* is quickly raised until the potassium hydroxide solution fills the burette and part of the reservoir above *E*; *E* is then closed, the bulb lowered and *D* opened. The gas is allowed to bubble up through the burette of alkaline solution at the rate of one bubble per second, by carefully opening *C*. The carbon dioxide is satisfactory for use when the bubbles are so small as to be almost invisible; in this condition they will rise in the burette at the approximate rate of 0.5 cm. per second. It is advisable to have a light in a fixed position behind the burette, since the apparent size of the bubbles varies, according to the illumination. If the bubbles are too large, or become too large in subsequent generations of gas by heating *P*, it will be necessary to re-evacuate the generating system as described above. After some of the bicarbonate has been used, it will be found necessary to heat the tube *P* a

short time before opening *B*, to prevent the mercury from sucking back into *R*, owing to the low pressure. Hence *B* must be opened cautiously until it is found that the pressure is the same on both sides; the carbon dioxide may then be generated at will. If the apparatus is to remain unused for some time with carbon dioxide in *T*, it is advisable to close *A*. In any event, stopcocks *A*, *B*, and *C* must be carefully cleaned and greased.

5. Analysis

The combustion tube, *G*, must be burned out before it can be used for analysis. It is well to fill that part of *G* that is normally occupied by the sample *K* and the copper oxide gauze *J* with finely ground copper oxide which is later used to mix with the sample. The tube is swept out with carbon dioxide passed at the rate of one bubble per second. This is done by opening *C* the required amount, *D* and *E* being wide open. After five minutes, the carbon dioxide is tested for complete absorption as previously described. If the bubbles are small enough (if they are not small enough the burette is emptied by opening *E* so as not to exhaust unnecessarily the potassium hydroxide, and sweeping is continued until all the inert gas has been removed), covers are placed on *G*, and the tube is heated with wing-top burners so that the supporting iron is maintained at dull red heat for an hour. The tube is again swept out and the size of the bubbles tested; if they are not small enough heating is continued until they are. The burners are then shut off and the covers removed to effect quick cooling; *D* is shut and *C* is opened so that the tube cools in an atmosphere of carbon dioxide.

While the tube is cooling, a 20–30 mg. sample is weighed out accurately to 0.1 mg. in a small (5 gm.) weighing bottle. When the combustion tube is cool enough to handle, it is disconnected at *H* (after shutting *C*) and the charge of copper oxide removed. To the sample in the weighing bottle is then added a 1 cm. layer of fine, previously ignited copper oxide; the bottle is shaken until thorough mixing has been effected. A layer of 0.5 cm. of copper oxide is put into the tube *G* and the sample mixture carefully poured in while the tube is held in a vertical position, so that none of the sample adheres to the sides (funnel tube). The weighing bottle is then washed three times with copper oxide (say a 0.3 cm. layer each time) and the washings added to the tube. The roll of copper oxide gauze, which has been reoxidized by heating it to red heat in a Bunsen flame and allowing it to cool in the air, is then slid into the tube; the latter is shaken to distribute the sample evenly over a 5 cm. length of the tube. *G* is now connected to *H* and then to *C*, swept out until the bubbles are small enough (this takes about five minutes) and the carbon dioxide shut off at *C*. The burette is filled and heating is begun, *D* being left open. Sections *L*, *M*, and *N* are heated strongly with two wing-top burners, or a long burner if available, and the tube above them is covered. Section *J* is then heated with a low flame which is gradually increased until the sample starts to burn. This should take about 10 min.

The tube should be heated at such a rate that the bubbles come over not faster than one every two seconds; the heat is gradually increased to its maximum, and finally a cover is placed over the end of the tube next the stopper. Heating is continued until bubbles cease to appear in the burette (about 40 min.). *C* is now opened and the nitrogen remaining in the tube is swept over into the burette at the rate of one bubble per second until the bubbles are of the same size as they were before the burning. This takes approximately 20 min. Then *D* is shut, the burners are turned off, and the covers removed. The tube will be cool enough for another run in 30 min. *C* should always be shut when *G* is cool, to prevent loss of carbon dioxide through leakage at the rubber connections. (The above times are approximate, since some samples are more difficult to burn than others, and hence will require a longer time.) The percentage of nitrogen in the sample is calculated in the usual manner.

Whenever the apparatus is to stand unused for more than a day, the burette and leveling bulb are emptied and rinsed with water. They are left filled with water until the apparatus is to be used again, otherwise the stopcock *E* is liable to "freeze"; *E* should be cleaned and greased frequently.

The copper oxide in which the sample has been burned is saved after removal from the tube and re-used.

6. Sources of Error

For convenience a 20 mg. sample that contains 10.0% nitrogen will be considered. The greatest source of error in the determination is incorrect weighing of the sample, *e.g.*, an error of 0.2 mg. will give a value of 10.1 or 9.9% N, depending upon whether the error is positive or negative. Care must be taken that none of the sample is lost in transferring it from the weighing bottle to the combustion tube, and that none of it sticks to the end of the tube that is unheated.

An error of 0.02 cc. in reading the volume of gas evolved will cause an error of 0.1% in the value, *i.e.*, 10.1 or 9.9% N. A water-jacketed burette is an unnecessary refinement since it takes an error of 2° C. to give a value of 10.1 or 9.9% N., and it makes the graduations harder to read.

If the bubbles are not small enough the generator must be evacuated again or the potassium hydroxide solution must be renewed. When the apparatus is running properly a blank is not necessary, since it amounts to not more than 0.02 cc. of gas. A high grade sodium bicarbonate should be used. Some samples labeled c.p. do not give pure carbon dioxide. This necessitates a blank determination.

If the tube is not heated sufficiently at the end *MN*, carbon monoxide may escape combustion and thus introduce an error.

Some of the values found in routine analyses are given in Table I.

TABLE I
PER CENT NITROGEN FOUND IN ANALYSES BY THE METHOD DESCRIBED

Substance	Empirical formula	Calcd., %	Found, %
Diphenyldipyrrol	$C_{20}H_{18}N_2$	9.8	{ 9.8, 9.7 9.8, 9.8*
Diphenyldipyrrol picrate	$C_{28}H_{21}O_7N_8$	13.6	
Diphenyldipyrrol methiodide	$C_{21}H_{21}N_2I$	6.5	
2,4-Dinitrophenylhydrazones of			
Butyrophenone	$C_{18}H_{16}O_4N_4$	17.1	17.1
β -Benzoylpropionic acid	$C_{18}H_{14}O_6N_4$	15.6	15.7
Dimethylcyclopentene aldehyde	$C_{14}H_{14}O_4N_4$	18.4	18.4
Substance A	$C_{29}H_{22}O_5N_4$	10.7	10.5
Substance B	$C_{30}H_{28}O_7N_4$	10.1	10.0
Substance C	$C_{29}H_{22}O_5N_4$	11.1	11.1, 11.1
Di-dinitrophenylhydrazones of			
Acetylacetone	$C_{18}H_{18}O_5N_8$	23.6	23.4, 23.5
Dibenzoylthane	$C_{28}H_{22}O_8N_8$	18.7	18.5

* Three different operators.

Acknowledgments

The writers acknowledge their indebtedness to the many graduate students whose experience over a period of years has been incorporated into this work. Valuable suggestions have been made by Drs. J. A. Scarrow, G. W. Wright and Mr. R. V. V. Nicholls. The glass blowing was done by Mr. L. F. Halley.

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FATTY ACIDS AND THEIR ESTERS

I. SOME OBSERVATIONS ON THE CRYOSCOPY AND EBULLIOSCOPY OF FATTY ACIDS¹By H. N. BROCKLESBY²

Abstract

By the ebullioscopic method and in benzene solution, saturated fatty acids show, with increasing carbon content, a decreasing degree of association up to lauric acid, after which it remains more or less constant. Unsaturation is shown to decrease the extent to which the molecules of fatty acids of the same carbon content associate. The degree of association of oleic acid in several solvents has also been determined.

The work recorded in this series of papers was undertaken as a contribution to the study of the properties of the naturally occurring unsaturated fatty acids and their esters, with particular reference to reactions involving polymerization and isomerization. Considerable time has been spent in examining experimentally those methods generally used in the investigation of polymerized unsaturated esters, since many of the apparent contradictions in the literature of this subject appear to be due to the improper use or interpretation of the data obtained by various procedures. During a study of the association theory of polymerization some observations were made regarding the cryoscopic and ebullioscopic behavior of solutions of pure acids and esters, the results of which are summarized in the present paper. Subsequent papers in this series will describe other aspects of the investigation including the following: the molecular weights of polymerized esters, the bromine vapor method of iodine value determination, the ultra-violet irradiation of methyl linolate, the action of some reagents on polymerized esters and the isomerism and thermal polymerization of methyl linolate.

The Variation of the Ebullioscopic θ/M with a Homologous Series of Fatty Acids in Benzene

The association of aliphatic acids has been known for some time. By means of X-ray studies, Müller and Shearer (16) and Trillat (21) have shown that the crystal unit of solid fatty acids is made up of two molecules arranged with their free acidic groups towards each other. Morrow (15) has indicated that the liquid fatty acids also show evidence of this type of orientation. Bury and Jenkins (3) and others have studied the behavior of acetic acid in various solvents, and the bimolecular nature of this acid has been well established. The association of the higher fatty acids is also well known, but only recently

¹ Manuscript received March 9, 1936.

Contribution from the Pacific Fisheries Experimental Station, Biological Board of Canada, Prince Rupert, British Columbia, Canada. Some of the data included in this series were taken from a thesis submitted by the writer to McGill University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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has the effect of the length of the carbon chain on this association been investigated. Assuming the theoretical molecular weight for the dissolved acids, Francois (6) found that the molecular depressions of the freezing points in benzene and nitrobenzene solutions increased with increasing carbon content of the fatty acids up to the C_{14} member, after which the values remained constant. Boutaric and Roy (1) recalculated Francois' results to show the change in association of the acids by assuming constant molecular depression for the solvents. Recently Broughton (2) found a discontinuity in the degrees of association of the saturated fatty acids by cryoscopic determinations in cyclohexane. This author found a minimum at C_{12} (lauric acid); as the number of carbon atoms increased above this value the degrees of association apparently increased. Discontinuities in other properties of the fatty acids have been noted by Lee and van Rysselberge (9), Nietz (17), Randall, McBain and White (18) and others.

In connection with other investigations being made in these laboratories, it was desired to extend the observations of Broughton to higher members of the series of fatty acids. However, the low solubilities of the higher acids in cyclohexane and benzene at the freezing point limit the data that can be obtained by the cryoscopic method, and observations were therefore made by the ebullioscopic method of Menzies and Wright (14). Most of the work was done with benzene as solvent. The data are given in Table I and shown

TABLE I
VARIATION OF EBULLIOSCOPIC θ/M WITH HOMOLOGOUS SERIES OF FATTY ACIDS IN BENZENE

Acid	Mols per kg.	θ	θ/M	Acid	Mols per kg.	θ	θ/M
Caprylic	0.0598	0.0886	1.499	Palmitic	0.0211	0.0422	1.997
	0.1032	0.1470	1.424		0.0884	0.1581	1.787
	0.1420	0.1909	1.345		0.1188	0.2084	1.754
Capric	0.0504	0.0844	1.674		0.1530	0.2643	1.727
	0.1280	0.2009	1.569		0.1883	0.3232	1.716
	0.1724	0.2624	1.522	Stearic	0.0260	0.0503	1.937
Lauric	0.0507	0.0977	1.927		0.0568	0.1035	1.823
	0.0767	0.1428	1.862		0.0837	0.1472	1.759
	0.0940	0.1710	1.819		0.1152	0.1992	1.729
	0.1354	0.2395	1.770		0.1538	0.2605	1.693
	0.1841	0.3189	1.732	"Arachidic"*	0.0536	0.1018	1.899
Myristic	0.0528	0.0982	1.859		0.0677	0.1246	1.840
	0.1226	0.2117	1.726		0.0805	0.1450	1.801
	0.1463	0.2446	1.672		0.1044	0.1830	1.753
	0.1905	0.3178	1.668				

* The sample of "arachidic acid" was obtained from a reliable chemical company. After resaponification and recrystallization it had a constant melting point of 73.2°C . and a neutralization equivalent of 353. Pure arachidic acid melts at 77°C . and has a neutralization equivalent of 312.2. The specimen used consisted of a mixture of arachidic and lignoceric acids. The experimental value for the neutralization equivalent was used in calculating the molarity.

graphically in Fig. 1. It is evident from these data that even at the boiling point the degrees of association of the acids decrease with increasing carbon content up to lauric acid. However, the values of θ/M for the higher members do not show a consistent lowering, and it appears probable that at the boiling point the minimum association occurs at C_{12} and remains constant at higher carbon contents. The differences between the values of θ/M for

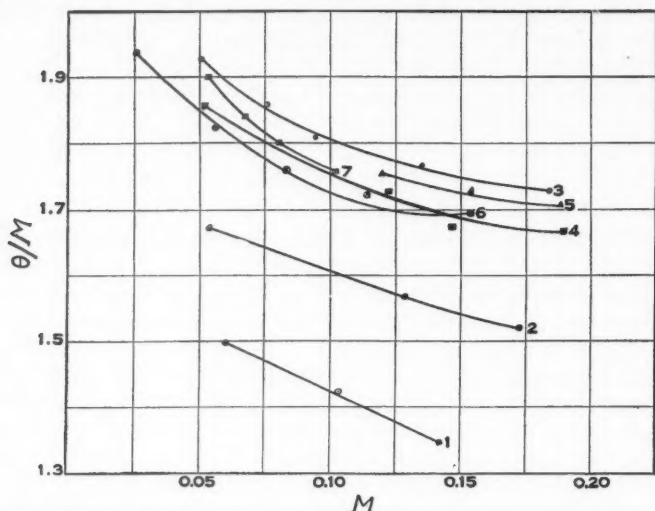


FIG. 1. Influence of carbon content on values of θ/M for saturated fatty acids in benzene. Legend: 1. Caprylic acid. 2. Capric acid. 3. Lauric acid. 4. Myristic acid. 5. Palmitic acid. 6. Stearic acid. 7. "Arachidic acid."*

the fatty acids higher than lauric approach the limits of the experimental error of the method (about 1 in 200), and thus cannot be interpreted in terms of differences of association. Observations with cyclohexane solutions show similar results, with the possibility of a shift of the minimum association to C_{16} . More precise measurements of this kind are beyond the scope of these laboratories, but if substantiated the data would be of value, particularly in their relation to the discontinuities of other properties of the higher fatty acids.

The Effect of Unsaturation on the Association of Aliphatic Acids

To the writer's knowledge no observations have been recorded on the effect of unsaturation on the association of aliphatic acids. One ethylene bond in the 9,10 position of a C_{18} acid has a pronounced effect on some of the physical properties, as exemplified by stearic and oleic acids; the melting points and boiling points are 71 and 14° C., and 291 and 286° C. (at 100 mm.) respectively. Unsaturation appears to weaken the cohesive force. Ives,

* See footnote to Table I.

Linstead and Riley (8) have recently redetermined the dissociation constants of a number of simple olefinic acids. With very few exceptions the unsaturated acids they investigated were either as strong as, or stronger than, the saturated acids with the same carbon skeleton. From their work, however, it would appear that when the double bond has receded more than three or four carbon atoms from the carboxyl group, the effect of this bond on dissociation is negligible. This is not true of the effect on association.

In determining θ/M with three acids of the C_{18} series (stearic, oleic and linolic) by cryoscopic and ebullioscopic methods, it has been found that in every case the highest value is given by the most unsaturated acid, thus indicating the decrease in association with increase of unsaturation. These data will be found in Tables II and III. In the latter, the values of θ/M for the three acids in boiling cyclohexane are given, and these data indicate that the effect of the double bond on association is accumulative. It was thought that *cis-trans* isomerism might play some part in this phenomenon, but the values of θ/M for oleic and elaidic acids are substantially the same. In the absence of any data on the effect of unsaturation on association and/or co-ordination, the only explanation which can be given for this phenomenon must be based on the rigidity of the unsaturated bond. In saturated acids the molecules must be able to approach one another more closely than in the case of the unsaturated. Association and/or co-ordination is therefore facilitated in the former substances. Such an explanation admittedly does not take into consideration the possibility that double bonds may have a latent polarizability, but, as Ives, Linstead and Riley (8) have shown, this polarization is without effect on the carboxyl group when the double bond is three or four carbon atoms removed.

TABLE II

THE EFFECT OF UNSATURATION IN ALIPHATIC ACIDS ON θ/M IN VARIOUS SOLVENTS

Acid	θ	M	θ/M	Acid	θ	M	θ/M
<i>Cryoscopic</i>							
<i>Solvent: cyclohexane</i>				<i>Solvent: benzene</i>			
Oleic	.497	.0454	10.94	Oleic	.163	.0537	3.035
	.928	.0860	10.79		.356	.1201	2.964
	1.377	.1273	10.82		.455	.1541	2.953
	1.944	.1825	10.65		.828	.2837	2.919
Linolic	.059	.0046	12.09	Elaidic	.259	.0861	3.008
	.175	.0155	11.23		.356	.1205	2.954
	.380	.0339	11.21	Linolic	.164	.0525	3.123
	.734	.0661	11.10		.363	.1179	3.078
					.510	.1712	2.979
					.724	.2470	2.951

TABLE II—Concluded
THE EFFECT OF UNSATURATION IN ALIPHATIC ACIDS ON θ/M IN VARIOUS SOLVENTS

Acid	θ	M	θ/M	Acid	θ	M	θ/M
<i>Ebullioscopic</i>							
<i>Solvent: benzene</i>				<i>Solvent: chloroform</i>			
Stearic	.0503	.0258	1.946	Stearic	.1162	.0436	2.666
	.1035	.0565	1.831		.1820	.0707	2.574
	.1472	.0833	1.767		.2248	.0888	2.531
	.1992	.1147	1.737	Oleic	.1039	.0309	3.366
	.2605	.1531	1.702		.1337	.0431	3.102
Oleic	.0564	.0263	2.131		.1715	.0598	2.869
	.1023	.0530	1.929		.2141	.0770	2.779
	.1452	.0795	1.825		.2557	.0956	2.673
	.2504	.1428	1.754	<i>Solvent: carbon disulphide</i>			
	.3343	.1933	1.729	Stearic	.1253	.0994	1.260
<i>Solvent: carbon tetrachloride</i>					.1988	.1518	1.318
Stearic	.1228	.0388	3.164		.2818	.2166	1.301
	.1854	.0592	3.132	Oleic	.2283	.1704	1.340
	.2483	.0803	3.092		.3295	.2390	1.379
	.1217	.0345	3.528		.4434	.3307	1.341
Oleic	.1680	.0502	3.348	<i>Solvent: acetone</i>			
	.2127	.0669	3.176	Stearic	.1193	.0682	1.748
<i>Solvent: ethyl ether</i>					.1800	.1025	1.756
Stearic	.5924	.2765	2.153		.2282	.1314	1.737
	.8192	.3812	2.149		.2826	.1669	1.693
	1.056	.4901	2.155	Oleic	.1043	.0572	1.823
	.4153	.1896	2.190		.1557	.0875	1.778
Oleic	.6402	.2964	2.160		.2119	.1193	1.776
	.8938	.3995	2.237		.2764	.1576	1.754
	1.102	.4947	2.228				

TABLE III

THE VALUES OF θ/M FOR STEARIC, OLEIC AND LINOLIC ACIDS IN BOILING CYCLOHEXANE. CONCENTRATION, 0.03 MOLES PER KG.

Acid	Stearic	Oleic	Linolic
θ/M	1.688	1.731	1.818

The Association of Oleic Acid in Various Solvents

It is well known that, in general, organic acids exist in the monomeric condition in solvents of high dipole moment, but tend to form dimers in non-polar solvents of low dipole moment. In order to obtain more precise information concerning the association of naturally occurring acids in various common solvents, the association of pure oleic acid in various solvents has

been determined by both cryoscopic and ebullioscopic methods. This information was considered necessary for a further study of the association theory of polymerization.

The associations, α , shown in Table IV, were calculated by dividing the value of θ/M for the methyl ester by that of the free acid at equal molar concentrations, thus eliminating the disturbing influence of mass on the disassociation of the solvent used.

TABLE IV
THE ASSOCIATION OF OLEIC ACID IN VARIOUS SOLVENTS

M	θ/M (ester)	θ/M (acid)	α	M	θ/M (ester)	θ/M (acid)	α
<i>Cryoscopic</i>							
	<i>Solvent: benzene. d.p.m.* = 0</i>				<i>Solvent: cyclohexane. d.p.m. = 0</i>		
0.10	5.27	3.00	1.76	0.05	21.40	10.50	2.04
0.20	5.17	2.92	1.77	0.10	21.50	10.75	2.00
	<i>Solvent: acetic acid. d.p.m. 1.73</i>				<i>Solvent: dioxane. d.p.m. = 0</i>		
0.15	3.67	3.74	0.98	0.025	5.51	4.83	1.14
0.20	3.57	3.52	1.01	0.075	5.27	4.77	1.10
<i>Ebullioscopic</i>							
	<i>Solvent: benzene. d.p.m. = 0</i>				<i>Solvent: cyclohexane. d.p.m. = 0</i>		
0.07	2.81	1.86	1.51	0.04	2.76	1.77	1.56
0.10	2.75	1.79	1.53	0.08	2.73	1.72	1.58
	<i>Solvent: carbon tetrachloride. d.p.m. = 0</i>				<i>Solvent: chloroform. d.p.m. = 1.05</i>		
0.04	5.32	3.46	1.53	0.04	3.77	3.17	1.18
0.05	5.28	3.35	1.57	0.06	3.71	2.85	1.30
	<i>Solvent: carbon disulphide. d.p.m. = 0</i>				<i>Solvent: ethyl ether. d.p.m. = 1.12</i>		
0.10	2.46	1.30	1.89	0.20	2.27	2.19	1.03
0.20	2.45	1.37	1.78	0.40	2.30	2.20	1.04
	<i>Solvent: dioxane. d.p.m. = 0</i>				<i>Solvent: acetone. d.p.m. = 2.8</i>		
0.02	2.87	2.87	1.00	0.06	1.76	1.87	0.97
0.03	2.86	2.86	1.00	0.10	1.75	1.80	0.94

* Dipole moments ($\times 10^{18}$ e.s.u.). Taken from Appendix 1, "Dielectric constant and molecular structure," by C. P. Smyth. Chem. Cat. Co., New York. 1931.

The data serve to emphasize further the lack of concordance between the associating power of a solvent and its dipole moment. In acetic acid and dioxane the freezing point method indicates almost complete formation of

monomeric molecules of oleic acid, but the dipole moments of the two solvents are 1.73×10^{18} and 0 respectively. By the same method, oleic acid shows associations of 1.76 and 2.00 in benzene and cyclohexane solutions at a molarity of 0.1, although these two solvents both have zero dipole moment. In general, where the association of the solvent is high the disassociation of the oleic acid to the monomeric state is more complete, but even here there is an anomalous case. Ethyl ether with an association factor of 1 (11) is supposed to have a weak molecular field in spite of its permanent dipole (7). The data given in Table IV indicate however that in ether solution oleic acid exists almost completely in the monomeric state. It will be observed, however, that in all solvents containing an oxygen atom the oleic acid exists as a monomer, irrespective of the dipole moments or associations of such solvents. This fact seems to support Sidgwick's hypothesis and suggests that the unshared electrons of the oxygen in these solvents form co-ordinate links with the hydrogen of the carboxyl group in the oleic acid, thus reducing the co-ordination between the carboxyl groups themselves.

Methods

Experimental

Thy cryoscopic determinations were made in a closed-system Beckmann apparatus, automatic stirring being accomplished by means of a magnetic device. A stirring rate of 20 strokes per minute was used. The bath temperature was maintained constant at a temperature of 2° C. ($\pm 0.25^\circ$) lower than the freezing point of the solvent employed.

The ebullioscopic determinations were made with a Menzies and Wright apparatus (14); a differential thermometer filled with water was employed. Two small amethysts were used to facilitate uniform boiling. Heating of the solvent was accomplished by means of a small enclosed electric heater so arranged on a swivel device that it could be easily and quickly swung away from the boiling tube. This heater was so constructed that the only appreciable heat was directly on the bottom of the boiling tube, and superheating of the solvent vapors was eliminated. The differential thermometer and the Cottrell pump were held at the same height by means of a large perforated rubber stopper which sat lightly on the top of the condenser. The readings of the volume of solvent and the height of the menisci of the thermometer were made with a small lens and a suitable lighting arrangement. The rate of boiling and consequently the height to which the solvent vapors rose in the condenser was accurately controlled by a variable resistance in series with the heater. When dioxane was used as a solvent the condenser water was maintained between 10 and 12° C. to prevent the solvent from crystallizing on the sides of the condenser. Solutes, when liquid, were added from a tared weighing bottle by means of a capillary pipette fitted with a small rubber bulb. Solids were added in the form of pellets from a tared watch glass with the aid of a platinum rod.

In calculating the temperature from the observed readings on the differential thermometer a corrected factor was always used. This was cal-

culated by adding to the boiling point of the pure solvent half the ebullioscopic rise obtained by means of a preliminary factor. The tables of vapor pressures used were those of Menzies (14). The boiling points of the pure solvents were determined at the beginning of each set of determinations by means of a total-immersion Fisher thermometer.

Materials

All materials used were the purest obtainable, but in each case they were repurified by the most suitable method. In calculating molarities the experimental values for the molecular weights were used.

Acids

Caprylic. M.p. 14.5° C. Neut. equiv.: calc. 144.1; found 143.9.

Capric. Recrystallized from acetone. M.p. 32.0. Neut. equiv.: calc. 172.1; found 172.3.

Lauric. Recrystallized six times from alcohol and once from acetone. M.p. 42.5. Neut. equiv.: calc. 200.6; found 200.3.

Myristic. Recrystallized five times from alcohol and once from acetone. M.p. 53.7. Neut. equiv.: calc. 228.3; found 226.8.

Palmitic. Recrystallized seven times from alcohol and once from acetone. M.p. 62.5. Neut. equiv.: calc. 256.3; found 255.7.

Stearic. Recrystallized seven times from alcohol and once from acetone. M.p. 69.6. Neut. equiv.: calc. 284.3; found 282.9.

Oleic. Prepared from beef tallow fatty acids by lead salt separation followed by recrystallization of lithium salts from alcohol. Iodine value: calc. 90.1; found 89.5. Neut. equiv.: calc. 282.3; found 282.1.

Linolic. Prepared from liquid fatty acids of cotton seed oil through isolation of tetrabromstearic acid (M.p. 113° C.) and reduction with zinc in absolute methyl alcohol. Iodine value: calc. 181.2; found 179.6.

Elaidic. Prepared from the oleic acid as above by Poutet's reagent. Iodine values and neutralization values of the recrystallized product remained the same as those for oleic acid.

Esters

Methyl oleate was prepared from the above-mentioned oleic acid by esterification with c.p. absolute methyl alcohol in the usual manner. The neutral ester was purified by vacuum distillation.

Solvents

Benzene. A c.p. thiophene-free product was purified by Richards and Chadwell's method (19) and frozen out five times to a constant melting point.

Cyclohexane. A c.p. grade was repurified by Richards and Chadwell's method and frozen out four times to constant melting point.

Acetone. The constant boiling point fraction of a c.p. product was recrystallized with sodium iodide according to the method of Shipsey and Werner (20) (see Lochte *et al.* (10)). The pure product was kept over "anhydron" from which it was distilled immediately before use.

Dioxane. A c.p. product was repurified by Eigenberger's method (5). After fractional distillation the product was frozen out three times to constant melting point.

Anhydrous glacial acetic acid was prepared from a c.p. product by the use of boron triacetate, according to Eichelberger and LaMer's method (4).

The other solvents used in this investigation were of the best grade obtainable, and were all repurified by standard methods as given by McArdle (12).

Acknowledgments

The writer wishes to take this opportunity to thank Dr. H. Hibbert, Professor of Industrial and Cellulose Chemistry, McGill University, for his encouragement and advice during the course of the work; and to acknowledge the technical assistance of Mr. K. H. Harding and Mr. V. Thomas in obtaining some of the data reported in this paper.

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FATTY ACIDS AND THEIR ESTERS

II. MOLECULAR WEIGHTS OF POLYMERIZED ESTERS¹BY H. N. BROCKLESBY²

Abstract

When a value of K that allows for the effect of the solute on the dissociation of the solvent is used, raw linseed oil shows normal values for the molecular weight when determined cryoscopically or ebullioscopically in a number of diverse solvents. Similarly, polymerized oils and esters show identical molecular weights in different solvents when determined either cryoscopically or ebullioscopically. The data indicate that polymerized esters of unsaturated fatty acids cannot be assumed to be associated.

A resume of the literature shows a great variation in the cryoscopic and ebullioscopic values reported for the molecular weights of fatty oils and their thermal polymers. These variations, in the main, have been ascribed to the association of the solute, and this explanation has been largely responsible for the association theory of polymerization of fatty oils. Bauer (1) explains the discrepancies on the above basis, and shows that, in benzene, fatty acids are bimolecular whilst in camphor they are monomolecular. Wolff (12) interprets the variations as indicating the existence of "extra-molecular" linkages by means of which thickening of heated oils takes place, rather than through true polymerization. Wolff maintains that in camphor solution no increase of molecular weight is observed when oils or their fatty acids are polymerized by heat, while in benzene and chloroform the molecular weights increase with time of heating. On the other hand, Kino (7) and others have regularly reported increases in molecular weight of thermally polymerized esters when determined by means of the camphor method. Seaton and Sawyer (11), Morrell (9), Friend and Alcock (5) and others have shown that a lowering of the observed molecular weight occurs when the concentration of linseed oil or its polymers is increased in benzene solution. Such solutions showed values ranging from 930 at 9.5% concentration to 730 at 8.4% for linseed oil. In stearic acid, on the other hand, values are obtained which are independent of concentration, but which are much below the theoretical value for linseed oil.

Long and Wentz (8) determined the molecular weight of a linseed oil in benzene, nitrobenzene, ethylene bromide, bromoform, diphenyl ether and paracresol after heating it for one and a half and three hours. Whilst comparable results were obtained for any one solvent, the variations between the values obtained with the different solvents were large. Cutter (3) in reviewing these data interprets them as favoring the association theory for polymerized oils.

¹ Manuscript received March 9, 1936.
Contribution from the Pacific Fisheries Experimental Station, Biological Board of Canada, Prince Rupert, British Columbia, Canada.

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In a recent paper Gay (6) expressed the view that natural oils and their polymers are not associated, and that the variations noted in the literature are due to the dissociation of the solvent used. Using the cryoscopic method, Gay showed that with inert cyclohexane theoretical values for the molecular weight of raw linseed oil are obtained, and that there is no variation of the molecular weight with concentration for either the raw oil or its polymers. He thus concludes that such polymers have a definite composition and molecular weight.

Gay's observations are substantially in accord with those made in these laboratories. However, it was considered possible that even though polymers of unsaturated oils may be associated they would not undergo any appreciable dissociation by virtue of solution in the inert cyclohexane*, and therefore Gay's conclusions might be erroneous. It appeared necessary to show that, even with a dissociating solvent, dissociation of the polymerized oil does not take place.

Before examining the data obtained with polymerized esters, it is desirable to consider briefly the effect of solute concentration on θ/M (or K) with the solvents employed. The value of θ/M for any non-associated solute in a given solvent is not entirely independent of the concentration. In the case of non-associated inert solvents this variation may be so small as to be negligible when the value is used for molecular weight measurements. On the other hand, with associated solvents the value of θ/M may vary over a considerable range, and the use of an arbitrary constant may cause serious errors in the results. There is some doubt as to the validity of the mass law when applied to association (4, 10), and for precise molecular weight work it appears necessary to determine the values of θ/M over the necessary concentration range with a suitable non-associated solute. In the present case this was done with pure methyl oleate in several of the more commonly used solvents. The data are given in Table I. As might be expected, cyclohexane showed virtually no variation of θ/M with change in solute concentration. Dioxane by the cryoscopic method and acetone by the ebullioscopic gave values which fell linearly with concentration. In the case of benzene, however, the relation was not linear, and it is presumed that there are two opposing effects, dissociation of the solvent and solvation, resulting in a maximum or minimum as the case may be. The value of θ/M in carbon tetrachloride is virtually unaffected by change in solute concentration above a concentration of 0.7%. It is evident that in the determination of the molecular weights of highly polymerized esters and acids, appreciable variations in the value of θ/M will greatly affect the results, and the choice of the solvent and determination of the proper cryoscopic or ebullioscopic constant are of great importance. It may also be added that in the case of solvents that are difficult to prepare in a state of absolute purity, *i.e.*, cyclohexane, carbon tetrachloride, etc., it is better to plot a K -concentration curve for each new lot of solvent. In

*Unpublished data from these laboratories showed that associated dioxane did not undergo any appreciable dissociation at low concentrations in cyclohexane, as indicated by the cryoscopic method.

TABLE I
VARIATION OF θ/M WITH CONCENTRATION USING METHYL OLEATE AS SOLUTE

Conc., %	M	θ	θ/M	Conc., %	M	θ	θ/M	Conc., %	M	θ	θ/M
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Cryoscopic

Solvent: dioxane				Solvent: cyclohexane				Solvent: benzene			
0.782	0.0264	0.128	4.847	0.189	0.0064	0.137	21.33	0.689	0.0269	0.155	5.749
1.720	0.0582	0.273	4.687	0.318	0.0107	0.233	21.65	2.090	0.0707	0.418	5.913
3.760	0.1270	0.565	4.447	0.803	0.0273	0.585	21.43	3.700	0.1252	0.769	6.140
3.781	0.1277	0.562	4.400	1.430	0.0486	1.041	21.39	4.980	0.1683	1.101	6.538
6.130	0.2070	0.871	4.207	2.420	0.0822	1.177	21.53	6.910	0.2336	1.321	5.655
								6.860	0.2996	1.704	5.680
								10.28	0.3474	1.971	5.670
								11.51	0.3889	2.175	5.590
								13.50	0.4561	2.537	5.562
								15.30	0.5180	2.860	5.520

Ebullioscopic

Solvent: cyclohexane				Solvent: carbon tetrachloride				Solvent: dioxane			
0.906	0.0335	0.916	2.734	0.672	0.0230	1.255	5.458	0.358	0.0121	0.3460	2.864
1.527	0.0565	1.537	2.721	0.899	0.0304	1.593	5.252	0.758	0.0249	0.7345	2.947
2.316	0.0857	2.387	2.786	1.054	0.0354	1.864	5.274	1.076	0.0363	1.1090	3.053
3.115	0.1153	3.169	2.749	1.241	0.0416	2.205	5.296	1.420	0.0479	1.4070	2.934
3.333	0.1233	3.424	2.776	1.427	0.0479	2.536	5.299				
				1.763	0.0591	3.101	5.245				
Solvent: acetone				Solvent: benzene							
2.600	0.0877	1.510	1.721	0.387	0.0131	0.390	2.983				
3.68	0.1243	2.089	1.680	0.785	0.0265	0.750	2.831				
5.84	0.1971	3.215	1.631	1.641	0.0554	1.524	2.751				
8.40	0.2836	4.305	1.518	2.145	0.0724	1.980	2.735				
0.47	0.3535	5.298	1.499	2.675	0.0903	2.421	2.682				
2.87	0.4343	6.263	1.442	3.394	0.1146	3.104	2.709				

the writer's experience such solvents give the same type of curve in each case, but the actual values may vary slightly. The application of the above principle to the association theory of polymerization will now be considered.

A linseed oil and its thermal polymer were examined cryoscopically and ebullioscopically in some of the solvents mentioned above, the value of K used being that found with methyl oleate at the appropriate concentration. The data obtained are given in Table II. When the correct constant thus ascertained is used, cyclohexane gives, by both methods, values for raw linseed oil that approach the theoretical (870-890), as also does acetone by the ebullioscopic method. With the other solvents, however, the results are lower than the theoretical but closer to it than the values usually reported. Whatever the cause of these low results, it is not confined to the raw oil alone. When the ratio of the molecular weight of the polymer to the molecular

TABLE II
MOLECULAR WEIGHTS OF RAW AND POLYMERIZED LINSEED OILS IN VARIOUS SOLVENTS

Raw linseed oil				Polymerized linseed oil				Average ratio Mol. wt. polym.
Conc., %	θ	K	Mol. wt.	Conc., %	θ	K	Mol. wt.	Mol. wt. raw oil
<i>Cryoscopic</i>								
<i>Solvent: cyclohexane</i>								
1.237	.293	207.7*	877	1.188	.178	207.7	1387	1.56
2.161	.522	207.7	859	1.718	.260	207.7	1373	
2.804	.656	207.7	887	2.445	.372	207.7	1365	
				3.088	.478	207.7	1342	
				4.102	.644	207.7	1323	
<i>Solvent: dioxane</i>								
3.726	.248	44.55	666	5.931	.250	42.25	1002	1.50
6.030	.382	42.20	669					
<i>Solvent: benzene</i>								
8.698	.620	56.80	797	4.383	.273	65.21	1047	1.36
10.590	.769	55.90	770	6.373	.335	56.51	1075	
12.179	.896	55.60	755	8.256	.437	56.80	1073	
				10.418	.560	56.71	1055	
<i>Ebullioscopic</i>								
<i>Solvent: cyclohexane</i>								
0.699	0.226	27.53	851	1.111	.218	27.53	1405	1.52
2.729	0.870	27.53	864	1.978	.409	27.53	1330	
5.251	1.209	27.53	841	3.119	.658	27.53	1304	
				4.108	.893	27.53	1266	
<i>Solvent: carbon tetrachloride</i>								
1.116	.723	52.82	816	1.193	.514	52.92	1228	1.49
1.428	.937	52.99	807	1.558	.675	52.87	1222	
1.641	1.040	52.68	836	1.819	.776	52.25	1225	
<i>Solvent: acetone</i>								
2.665	.525	17.06	866	2.742	.353	17.06	1326	1.52
4.859	.915	16.50	876	4.571	.562	16.59	1349	
7.892	1.399	15.70	886	6.383	.769	16.10	1335	
11.282	1.903	14.81	878	12.241	1.336	14.58	1336	
<i>Solvent: benzene</i>								
1.759	.583	27.38	825	1.983	.374	27.20	1442	1.58
2.509	.791	26.85	851	2.811	.584	26.82	1292	
3.388	1.088	27.09	844	3.793	.839	27.55	1245	
4.019	1.307	27.88	857					

* The raw and polymerized linseed oils were examined cryoscopically in a new batch of cyclohexane, which in spite of careful purification gave a slightly lower value for K than that found for the previous batch, the values of which are reported in Table I.

weight of the raw oil (at approximately equal concentrations) is calculated for each solvent, remarkably concordant results are obtained. With the single exception of benzene by the cryoscopic method, the values of all these ratios fall within the range 1.49 to 1.58. Any dissociation of the polymer would tend to lower this value. In the previous paper of this series (2), the degree of association of oleic acid in the above-mentioned solvents was reported. It will be seen that there is no relation between the dissociating power of the solvent and the ratios given in Table II. For instance, according to the results obtained by the cryoscopic method, oleic acid appears to exist as the dimer in cyclohexane, but the results by the ebullioscopic method indicate that this substance exists in acetone as a monomer. Under similar conditions these two solvents give the theoretical value for raw linseed oil and substantially the same values for the polymerized oil. Similar comparisons may be made with the other solvents. Consistent results are also obtained with the methyl esters of polymerized fatty acids. For example, the polymerized linseed oil used in the above experiments was saponified, and the recovered free fatty acids were re-esterified with absolute methyl alcohol. The molecular weight of these neutral esters was then determined in three dissimilar solvents. The data given in Table III show consistent values for the molecular weight—a result that, in view of the differences in nature of the three solvents used, would not be expected if the polymerized esters were associated.

TABLE III

MOLECULAR WEIGHT OF METHYL ESTERS OF POLYMERIZED FATTY ACIDS IN VARIOUS SOLVENTS

Cyclohexane (f.p.)				Dioxane (b.p.)				Acetone (b.p.)			
Conc., %	θ	K	Mol. wt.	Conc., %	θ	K	Mol. wt.	Conc., %	θ	K	Mol. wt.
1.337	0.549	207.7	506	0.803	0.461	28.99	505	5.02	0.162	16.45	509

It therefore appears that polymerized esters cannot be assumed to be associated, at least not in the same sense as are hydroxylic substances. This conclusion is based on the assumption that methyl oleate itself is not associated, and that any change in θ/M (or K) with concentration is due to the dissociation of the associated solvent molecules. The data seem to indicate that this assumption is valid, particularly in view of the fact that the values for θ/M found when methyl oleate is used in various solvents agree with those recorded in the literature for simpler substances *over the same range of concentration*.

Methods

Experimental

The cryoscopic and ebullioscopic determinations were made by the methods described in the previous paper of this series.

Materials

Raw Canadian linseed oil was used in this work. The polymerized sample was prepared by heating the raw oil *in vacuo* at 300° C. for 12 hr. The raw and polymerized samples had the characteristics shown in Table IV.

TABLE IV

	Raw oil	Polymerized oil
Iodine value ($\frac{1}{2}$ -hr., Wijs)	174.8	126.0
Refractive index at 25° C.	1.4787	1.4846
Viscosity at 20° C., poises	0.4	3.69
Saponification value	187.8	—

For the preparation of the polymerized methyl esters, 500 gm. of the polymerized linseed oil was saponified with alcoholic potassium hydroxide, and the free fatty acids were recovered. These were dried and esterified with absolute methyl alcohol. After esterification the esters were washed five times with cold absolute methyl alcohol, and the last traces of free fatty acids washed out with dilute sodium bicarbonate. After removal of the solvent *in vacuo* the non-polymerized esters were evaporated off in a Hickmann still under a vacuum of 0.25 mm. and at a temperature of 150° C. The residue in the still was used in the above experiment.

Acknowledgment

The writer wishes to express his thanks to Mr. K. F. Harding and Mr. K. Green for their technical assistance.

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FATTY ACIDS AND THEIR ESTERS

III. IODINE VALUES BY THE BROMINE VAPOR METHOD¹BY H. N. BROCKLESBY² AND K. F. HARDING³

Abstract

A modified bromine vapor method for iodine value determination that allows of the determination of substitution is described. For non-conjugated unsaturated oils free from oxidation or polymerization products, values are obtained that are in close agreement with those found by Wijs' method. The unsaturation of conjugated esters can be determined satisfactorily. Owing to substitution, the unsaturation of oxidized or polymerized esters cannot be determined by this method.

The bromine vapor method for determining iodine values of oils possesses, in relation to other methods, certain advantages that have not been generally recognized. These advantages may be enumerated as follows: the method is cheap and requires but a small sample; in comparison with certain other methods, it is fairly rapid; complete saturation of normal and conjugated double bonds is obtained; as described later, substitution can easily be detected and, furthermore, does not take place with non-oxidized or non-polymerized oils and simple esters. On the other hand, several investigators have maintained that the method lacks accuracy; that with tung oil and other substances containing conjugated systems, absorption of bromine is incomplete, and that elimination of the excess bromine in the film cannot be achieved without substitution. Some time ago one of the writers (H. N. B.) developed a modification of this method. In view of recent publications on the subject a description of the modification is presented here, together with some results obtained.

The bromine vapor method has been developed chiefly through the work of Becker (2), Sabalitschka and Dietrich (11, 12), Toms (13) and Rossmann (9), the last-named extending its use to hydroxy compounds. Lévy (7) obtained the iodine value of raw and boiled tung oils by heating a thin film in bromine vapor, a procedure that might favor substitution. Jordan (6) maintains that the absorption of bromine vapor by tung oil is never complete unless liquid bromine is in contact with the film of oil, a circumstance that also leads to substitution. In a second communication on this subject Rossmann (10) described a titrimetric method in which bromine vapor is used, the principle being the reaction between a weighed quantity of bromine and the solid, liquid or gaseous test substance, followed by titration of the excess bromine. For gaseous or highly volatile materials this modification is valuable, but for fixed oils or esters the writers' modification appears to be simpler. (Since this article was written, a modified bromine vapor method has been described by Böeseken and Pols (3); this method differs considerably from the one described in the present paper.)

¹ Manuscript received March 9, 1936.
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Description of Modified Method

The chief features of this modified method lie in the determination of substitution during the reaction period, and the avoidance of substitution during removal of excess bromine from the film. From 10 to 30 mg. (if a microbalance is used, from 2 to 10 mg. are sufficient) of the oil or ester is spread in a thin film on the abraded surface of a tared microscope slide by means of a second slide. The weighed slide is then placed in the horizontal absorption tube (see Fig. 1), containing from 10 to 20 drops of dry bromine.

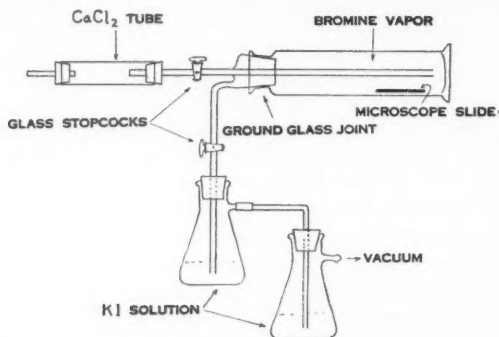


FIG. 1. Modified apparatus for determining iodine values by the bromine absorption method.

Absorption is allowed to proceed *in the dark* for 15 to 30 min. with substances containing no conjugated double bonds, and for one hour for those substances with conjugated double bonds. A current of clean dry air is then aspirated through the apparatus for 15 min., after which the potassium iodide traps are tested for hydrogen bromide in the usual manner by titration with sodium thiosulphate in the presence of potassium iodate and starch. The slide is then placed in a stout test tube and evacuated for five minutes at room temperature, after which it is placed in an Abderhalden drier and the evacuation continued until the slide comes to constant weight. A large number of experiments on a variety of oils and unsaturated esters have shown that the bromine remaining in the film after bromination and aeration does not substitute in the film material until a temperature of 90° C. or higher has been reached; the boiling liquid in the Abderhalden drier is chosen accordingly. The writers have used carbon tetrachloride for this purpose with satisfactory results.

Application of the Method

In Table I are given the iodine values of some natural oils and pure esters as determined by the Wijs, Rosenmund-Kuhnhehn and bromine vapor methods. With one exception none of the substances for which results are reported gave any substitution with bromine vapor, even when the absorption period was prolonged several hours. The exception was methyl linolenate,

which always shows a very faint trace of substitution. The writers have observed that when the acids (or their methyl esters) containing more than two double bonds are spread in thin films, their oxygen absorption is noticeable during weighing on a microbalance. As explained later this probably accounts for the trace of substitution that occurs in the presence of bromine vapor.

Schmidt-Nielsen and Owe* and others maintain that substitution occurs when Wijs' solution is allowed to react with fresh oils and esters, and it has been suggested that this is the reason Wijs values are always higher than those obtained by the use of pyridine sulphate dibromide. The data given in Table I would indicate that this is not necessarily true, as in most cases the Wijs values are slightly lower than the bromine vapor values which do *not* involve substitution. In the majority of samples examined the iodine value by the Wijs and bromine vapor methods are in good agreement. There are cases, however, where the two methods do not give concordant results. One example given in Table I is that of dogfish liver oil; with this oil, as in oils from related species, the Wijs values are always one or two units higher than the bromine vapor values. Another example of discordant results is seen in the case of methyl linolenate. Although not known to contain a conjugated system, this ester quite generally shows low absorptions by Wijs' solution. With bromine vapor or bromine in methyl alcohol, however, the absorption is much higher; but still lower than the theoretical value of 260.5.

With oils such as tung oil, containing conjugated esters, bromine vapor is absorbed without substitution, but a longer period of absorption is required. In this case there is also greater difficulty in removing the last trace of dissolved bromine from the film. Immediately the bromine vapor comes in contact with the film of tung oil, wrinkling takes place and a tough leathery film surface is developed which greatly retards the diffusion of the bromine from the film even *in vacuo*. The values reported in Table I for the bromine vapor absorption of tung oil are slightly higher than those found by hydrogenation, but since the hydrogenated fat still showed a slight unsaturation (one unit) the agreement is fairly good.

The bromine vapor method is valuable for following differential halogen absorptions. This is so by reason of the fact that iodine monochloride such

TABLE I
IODINE VALUES BY THE WIJS, ROSENMUND-KUHNHENN
AND BROMINE VAPOR METHODS

Sample	Wijs	Rosenmund-Kuhnenn	Bromine vapor
Olive oil	83.9	76.5	84.3
Cottonseed oil	111.0	105.2	110.8
Dogfish liver oil	116.6	109.3	115.2
Bean oil	135.1	124.0	136.1
Corn oil	122.2	113.8	123.1
Salmon body oil	128.2	120.9	128.4
Linseed oil	185.6	173.3	187.2
Pilchard oil	183.2	172.0	183.6
Tung oil	225.5*	—	227.7
Methyl oleate	83.9	—	84.0
Methyl linoleate	170.9	—	170.8
Methyl linolenate	221.6	251.4†	254.1

* By hydrogenation.

† Kaufmann.

* See Reference (1), p. 135.

as is contained in Wijs' solution only slowly saturates conjugated systems, but bromine vapor saturates them comparatively rapidly, although more slowly than it does non-conjugated systems. As an example, some data that were obtained with samples of methyl linolate irradiated with ultra-violet light* are given in Table II. No substitution was observed with any of the

TABLE II
IODINE VALUE OF IRRADIATED METHYL LINOLATE

Substance	Wijs	Bromine vapor
Fresh methyl linolate*	166.0	165.8 (No substitution)
Fresh methyl linolate irradiated 113 hr.	155.1	165.3 (No substitution)

* This sample contains some methyl oleate.

irradiated samples when acted on by bromine vapor. There appears to be only a small decrease in the iodine value of such samples when determined by the bromine vapor method, but a marked decrease in the case of the Wijs values.

Since substitution can be readily estimated by this modified bromine vapor method, it was hoped that it might prove of value in the determination of the true unsaturation of oxidized and polymerized oils. Subsequent experiments, however, showed that values obtained with such materials are of little practical use, although the data are valuable in other connections. The addition of bromine in the vapor state to thermally polymerized esters of linolic and linolenic acids is accompanied by immediate substitution. In Table III are

TABLE III
BROMINE VAPOR ON POLYMERIZED METHYL LINOLATE

Time of bromination, hr.	0.5	1	2	5.5	14
Iodine value from total amount of bromine absorbed	100.2	107.7	111.4	116.5	124.3
Substitution iodine value	55.9	53.4	70.5	83.3	105.7

given some values obtained on a sample of methyl linolate that had been polymerized *in vacuo* for 24 hr. at 280° C. For any one sample of polymerized ester, prolonged contact with bromine vapor gives a rapid rise of total bromine absorption during the first two or three hours, followed by a slower rise after that time. Substitution increases more rapidly than does total bromine absorption, and if the reaction time is prolonged the substitution value, as determined by the amount of hydrogen bromide evolved, will ultimately be in excess of the total bromine absorption calculated from the increase in weight of the film. These results are similar to those obtained by Buckwalter and Wagner (4) who found substitution values greater than addition values

* This effect is described in the following paper of this series.

during the bromination of unsaturated materials in various solvents. Similar results are obtained when polymerized oils are treated with bromine vapor, and for such materials the bromine vapor method of determining unsaturation has but little value.

A similar condition obtains with oxidized oils. It has already been observed that highly unsaturated fatty acids or esters always show a slight oxygen absorption during weighing of the film, with a consequent trace of substitution during bromination, and this effect is heightened with increasing oxidation. For instance, a sample of methyl linolate which showed an iodine value of 169.9 was weighed out in the usual manner and allowed to stand for seven days in a desiccator in which the air was frequently renewed. During this time it had absorbed 8.5% of oxygen. After an exposure of 15 min. to bromine vapor it had absorbed bromine equivalent to an iodine value of 31.3, and had evolved hydrogen bromide equivalent to an iodine value of 333.9. Whether the substitution observed in the case of polymerized esters and oils is due to incipient oxidation products caused by residual traces of oxygen in the oils and esters is not known, but it must be emphasized that the same substitution was found in many samples of pure methyl linolate that were freshly distilled into heavy glass tubes under a high vacuum preliminary to sealing off and heating in the polymerizing furnace.

This brief account gives some idea of the utility of the bromine vapor method. The method is not as convenient as volumetric methods, but, where it is necessary to work on a micro-scale, results that compare very favorably with Wijs values can be obtained. The method is of particular value in the case of substances containing a conjugated double bond, but cannot be used to determine the true unsaturation of oxidized and/or polymerized oils and esters.

Materials

Experimental

The oils used in this work were all fresh authentic samples. The methyl oleate was prepared from recrystallized lithium salts of the liquid fatty acids of olive oil. Methyl linolate and methyl linolenate were prepared from tetrabromostearic acid (m.p. 113° C.) and hexabromostearic acid (m.p. 180° C.), respectively, by a modification of Rollett's method (8).

Methods

Wijs, solution was made up according to Hunter and Hyde's method (5). For substances with an iodine value of 150 or less, a sample weight of 0.1500 ± 0.0005 gm. was used. For substances with an iodine value greater than 150, the sample weight was 0.1000 ± 0.0005 gm. Half-hour absorption periods were used.

Rosenmund and Kuhnhehn's method, outlined by Bauer (1), was followed. Sample weights and absorption times were the same as for Wijs' method.

In the bromine vapor method the microscope slides and films were weighed on a Kuhlmann microchemical balance. Titration for free hydrogen bromide

was made with $N/100$ sodium thiosulphate in the presence of potassium iodate and starch, after the free iodine liberated by the excess bromine had first been accurately titrated with $N/10$ sodium thiosulphate.

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